RESEARCHES

ON

THE ELECTRIC SYNTHESIS OF COLLOIDS

INAUGURAL DISSERTATION

BY

GÖSTA BÖRJESON, LIC. PHIL. VÄRML.

BY PERMISSION OF THE PHILOSOPHICAL FACULTY (NATURAL SCIENCE SECTION) OF THE UNIVERSITY OF UPSALA TO BE PUBLICLY DISCUSSED IN THE LECTURE HALL OF THE CHEMICAL INSTITUTION ON FEBRUARY 19th, 1921, AT 10 O'CLOCK A. M., FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

STOCKHOLM 1921
AKTIEBOLAGET FAHLCRANTZ' BOKTRYCKERI

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PREFACE.

The whole of the present work has been carried out at the Physical Chemistry Laboratory of the University of Upsala. The original suggestion was given to me by Professor Svedberg, who with never failing interest has generously offered both advice and co-operation. I hope that the work wil not prove unworthy of my friend and teacher.

I am obliged to Mr. Henry Alexander, Lecturer at the University of Upsala, for help from a linguistic point of view.

Motala, January, 1921.

The Author.

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PART I.

CHAPTER I.

Introduction.

1. *Forms of the Electric Synthesis of Colloids.* — Electrical energy has been employed in several methods for producing colloids. In this work we shall retain the term electric synthesis of colloids for those methods only in which the electric arc, surrounded by a liquid, is the means by which the electrode material is dispersed. The products obtained we shall briefly call electric colloids or electric sols. The production of the sols I have called dispersion or pulverisation.

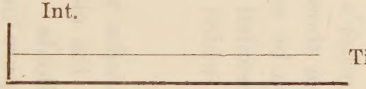
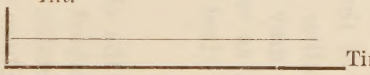
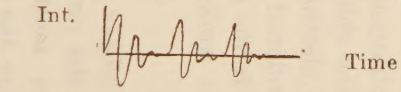
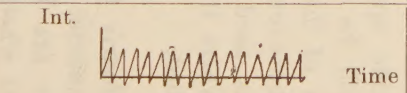
The methods of Bredig and Svedberg are well known, having found a wide application. The colloids obtained by Svedberg's method will be the chief subject of the author's investigations. But forms of the electric current other than those employed by the two above-mentioned scientists may also be used. Thus the author has used forms of current as represented in the scheme Table I, where the works are also cited in which these methods are described.

2. *Electric Colloids.* — Since the electrodes must be of conducting material the products obtained by the electric synthesis of colloids are in most cases metallic colloids. There may be some doubt whether the disperse phase is pure metal or whether some chemical compounds are formed by the action of the liquid employed. Scientists generally accept the opinion, however, that the bulk of the particles consist of metal, and later we shall see that this must be the case, at any rate when dispersed in organic liquids of indifferent properties.

Concerning the size of particles it is known that electric colloids are »polydisperse», i. e. the same sol contains particles of very different magnitudes[1]. The microscopic particles naturally

[1] R. Zsigmondy, Zur Erkenntnis der Kolloide, p. 147 (1905).

Table I.

Symbols of the colloids	Current	Graphic characteristics of the current	Authors and Literature	Remarks
C-sol	Continuous current		G. Bredig, Zeitschr. f. angew. Chemie, *1898*, 951. Zeitschr. f. Electrochem., *4*, 514 (1898). Anorganische Fermente (Leipzig 1901).	
S-sol	Continuous current		The Svedberg, Meddel. fr. K. Vetenskaps-akademiens Nobelinstitut, Band 5, N:o 10 (1919).	The arc is enclosed in a quartz-tube.
A-sol	Alternating current of low frequency		This work., section 30.	
O-sol	Oscillatory current		The Svedberg, Nova acta reg. soc. scient. Upsaliensis ser. IV. vol. 2, N:o 1.	
W-sol	Wave current		G. Börjeson and The Svedberg, Koll. Zeitschr. *25*, 154 (1919). This work, section 21. V. Kolschütter, Zeitschr. f. Electrochemie *25*, 309 (1919).	
I-sol	Intermittent current (of constant direction and intensity)		This work, section 29.	

soon fall to the bottom. With regard to the remaining portion Bredig[1] has stated, before the discovery of the ultramicroscope, that the particles of a gold sol obtained by C-current must be smaller than 0,14 μ in diameter. Burton[2] states gold and platinum hydrosols obtained by Bredig's method to be $2—6 \cdot 10^{-5}$ cm. in diameter. Svedberg[3] gives the dimensions of platinum particles in several liquids as 40—50 $\mu\mu$. Benedicks[4] thinks that almost all the mass of the dispersed metal consists of microscopic or nearly microscopic particles. This opinion, however, is not accepted by investigators of colloids, for they continue to employ the term colloids for the products in question.

It is apparent that the opinions of chemists on this subject are not in accordance. This is partly due to the fact that on account of the different size of the particles the subjective judgement finds a very large scope. Moreover, counting particles under the ultramicroscope is a very fallacious method when applied to polydisperse colloids, as a good many particles cannot be seen at all and as the number that can be discerned in a special case is in some degree dependent on the source of light employed. There are other circumstances too that may cause the discrepancy between the statements on this point. We shall return to this subject later on.

Apart from general descriptions of the colloids obtained by the electric methods which are to be found in the works cited above, there are very few researches published on the properties of electric sols. In the work now presented the author has not aimed at comprehensiveness but has found it necessary to put certain limits to the subject. He has therefore made a more intimate study only of those properties the knowledge of which might be of importance for the understanding of the very nature of the electric synthesis of colloids. As most characteristic properties can be ascribed to the size, consistency, structure, and shape of particles, and this will probably be the case with all of them in the future, it is evident that these properties should be studied one and all. So the principal subject of the author's investigations

[1] G. Bredig, Anorganische Fermente, p. 27 Lpzg (1901).

[2] Burton, Philos. Mag. **11** p. 425 (1906).

[3] The Svedberg, Nova acta soc. scient. Ups. Ser. IV, 2, N:o 1, p. 139 (1907).

[4] C. Benedicks, Kolloidchem. Beih. **4**. (1912).

has been the degree of dispersity. As far as possible the author has considered the consistency of particles, whereas their shape has not been the object of any particular attention. The author begs to call to mind that the particles visible under the microscope have already been studied rather thoroughly by C. Benedicks[1].

3. *Survey of Opinions as to the Electric Synthesis of Colloids.* — Several authors have attempted to give an explanation of the electric synthesis of colloids. The question, however, has not yet reached solution, i. e. a solution of a nature to be approved of by students of colloidal chemistry. Leaving out of consideration all chemical actions of the disperse medium (water, alcohol, ether etc.), which we are entitled to do since the metallic state of the disperse phase cannot be doubted, the author will give a short survey of opinions put forward on the subject. The chief question at first will be this: is the metal directly dispersed into the medium as ultramicroscopic particles or is there an intermediate state of gas into which it has to be transformed before producing the colloidal substance? In other words, is the electric synthesis of colloids a dispersion or a condensation method? On this point G. Bredig[2] already in 1898 expressed a very decided opinion. He says (with reference to his own method): »Sie beruht offenbar darauf, dass die Metalldämpfe des Lichtbogens in dem umgebenden kalten Wasser sofort als Nebel verdichtet werden». The opinion is apparently accepted by Freundlich[3] and Kohlschütter[4], who moreover applies the same view to Svedberg's oscillatory method. Accordingly the above-mentioned scientists consider the electric synthesis to be a condensation method.

The opposite opinion has found a representative in C. Benedicks[5], who has made a close study of the subject. He has arrived at the conclusion that the process in question is of a thermomechanic nature. According to him the particles are mechanically produced by the medium splitting the melted metal of the electrodes into globules of about microscopical size. To the vaporisation of metal Benedicks ascribes very little importance.

[1] Loc. cit.

[2] G. Bredig, Zeit. f. Elektrochemie, **4**, 514 (1898).

[3] H. Freundlich, Kapillarchemie, Lpzg, 1909.

[4] V. Kohlschütter, Die Erscheinungsformen der Materie, (1917).

[5] Loc. cit.

M. Koutscherow[1] has noted that a number of the metallic particles fall down to the bottom rather soon. The bulk of the particles are produced by some specific electrochemical action of the current. He considers that the formation of electric colloids is in a definite relation to the chemical valences of the metals used as electrodes. He also seems to hold that this process is one of dispersion.

Wo. Ostwald[2] too is of the same opinion as Benedicks in so far as he thinks that the metal is converted directly by dispersion into the colloidal state. As to the cause of this dispersion he proposes to introduce a new idea »the negative surface tension», which, according to him, would cause the dispersion of the metal in connection with the ordinary surface tension. The object of his discussion is to refer the electrolytical synthesis of colloids of Bredig and Haber[3] and others[4] and the electric synthesis of colloids to the same phenomenon. In point of principle, however, it seems impossible to deny that, owing to the negative surface tension, this dispersion really might give rise in certain cases to systems of molecular dispersity, i. e. in this case to vaporisation of the metal. And as he does not cite any experimental fact that might contradict such an assumption I cannot see that this theory contributes to the solution of the question raised above.

Now the opinions cited above have not taken into consideration a third eventuality. It may be possible that the electric synthesis of colloids is a dispersion as well as a condensation method. Such an opinion is put forward by Svedberg[5], and Nordlund[6], who has adopted the same view, has shown that such an assumption may very well agree with his experimental results. In addition Nordlund has suggested a picture of the process, which in more than one respect agrees with my own opinions (see Chapters VIII and IX).

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[1] M. Koutscherow, Koll. Zeit. **11**, 167 (1912).

[2] Wo. Ostwald, Koll. Zeit. **7**, 132 (1910).

[3] G. Bredig and F. Haber, Ber. Dtsch. Chem. Ges. **31** 2741 (1899).

[4] For the literature see The Svedberg, Die Methoden zur Herstellung kolloider Lösungen, 413, Dresden 1920.

[5] The Svedberg, Ber. **47**, 70 (1913).

[6] I. Nordlund, Inaug. Diss. 36—40 (1918).

The experimental results recently obtained by Svedberg[1] have caused him to adopt the opinion that the importance of the condensation process must be considerable.

4. *Plan of the present work.* — First the author will examine the sedimenting portion of sols obtained by the oscillatory method of Svedberg (O-sols). From this investigation it will appear probable that the dispersed metal consists of two distinct portions, the sedimenting coarse one and the residue. The author will therefore next devote a chapter to showing experimentally that the two portions mentioned above have different origins and a plausible explanation of their formation will be proposed. Having studied from the same point of view the disperse systems obtained by other forms of current the author will devote his investigations to the portion that does not sediment, i. e. the sols proper. The last chapter will contain a rather detailed discussion of the nature of the electric synthesis of colloids. This discussion will conclude with a description of the process in question such as the author conceives it.

[1] The Svedberg, Koll. Zeit **24**, 1 (1919).
» » Medd. K. Vet.-Akademiens Nobelinst. **5**, N:o 10, 15 (1919).

CHAPTER II.

Sedimenting Portion of O-sols.

Registering Increase of Sediment with Time and calculating the Distribution of Particles with regard to their Size.

5. *Theory.* On the basis of Stokes' law for globules falling in a viscous medium Schloesing père[1] has devised a simple method of calculating the mass of particles present within successive limits of the radius of particles from the weight of sediment registered at successive intervals of time. Applying the same law Odén[2] has published a graphical method of solving the same problem. Odén's method is theoretically more accurate. I have, however, considered a calculating method sufficient for my purpose.

Assume that at the time $t = 0$ metallic globules obeying Stokes' law are equally distributed in a liquid of known viscosity and specific gravity. At first let them all be of the same size. Since they fall at a constant rate the sediment on a plate near the bottom will also increase in weight at a constant rate until all the particles have reached the bottom. Let this be the case at the time t. This is the time needed for the particles at the surface of the liquid to reach the plate. Knowing the height of the liquid above the plate we can readily calculate the radius, r, of the particles.

Every value of t accordingly corresponds to a definite value of r.

Now let the particles be of various sizes. Then we can classify them in groups, each group containing particles of the same size equally distributed in the liquid. Consequently the rate of accumulation at each time, t, is a sum of accumulations of those groups of particles that have not yet completely

[1] Schloesing père, Compt. rend. **136**, 1608—1613 (1903); **137**, 369 – 374 (1903).

[2] Sven Odén, Bull. of Geol. Instit. of Upsala, Vol. XVI.

reached the plate. Until this moment these groups have all gathered on the plate at a constant rate, v. As the particles in question have been falling for the time t the weight of the part of them that is on the plate must be tv. Now consider those groups that have completely reached the plate at the same moment. The weight may be S. Let the total weight of the sediment be P. Then the following equation holds good:

$$P = S + tv \text{ or}$$
$$S = P - tv.$$

v can be approximately determined by observing the increase, $\triangle P$, of the weight for a short time, $\triangle t$, after the time t, i. e.

$$v = \frac{\triangle P}{\triangle t}; \text{ consequently}$$

$$S = P - t\frac{\triangle P}{\triangle t} \quad \ldots\ldots\ldots\

Then by applying the equation above we have

$$S = P - t_1\left(\frac{\triangle P}{\triangle t}\right)_1; \quad \text{(a)}$$

$$S + \triangle S = P + \triangle P - t_2\left(\frac{\triangle P}{\triangle t}\right)_2; \quad \text{(b)}$$

$\left(\frac{\triangle P}{\triangle t}\right)_1$ referring to the interval $\triangle t_1$, $\left(\frac{\triangle P}{\triangle t}\right)_2$ to $\triangle t_2$.

Replace t_1 by $t_2 - \triangle t_1$ in equation (a). Then

$$S = P - t_2\left(\frac{\triangle P}{\triangle t}\right)_1 + \triangle P;$$

$$S + \triangle S = P + \triangle P - t_2\left(\frac{\triangle P}{\triangle t}\right)$$

and by subtracting:

$$\triangle S = t_2\left[\left(\frac{\triangle P}{\triangle t}\right)_1 - \left(\frac{\triangle P}{\triangle t}\right)_2\right]; \quad \text{(2)}$$

$\triangle S$ being the weight of those particles the radii of which are limited by those values of r, r_1 and r_2 that correspond to t_1 and t_2.

The deduction above is not very different from that given by Schloesing père.

Let $\triangle t$ tend indefinitely towards zero.

Then equation (1) will be transformed into:

$$S = P - t\frac{dP}{dt} \quad \text{(1a)}$$

and equation (2) into:

$$dS = -t\,d\left(\frac{dP}{dt}\right) \quad \text{(2a)}$$

or after dividing by dt:

$$\frac{dS}{dt} = -t\frac{d^2P}{dt^2} \quad \text{(2b)}$$

The equations (1a) and (2b) are those found in Odén's work (l. c.)

Knowing the height h, specific gravity s, viscosity η of the liquid and the specific gravity $\triangle$ of the particles we obtain the values of r by applying Stokes' formula:

$$r = \sqrt{\frac{9}{2} \frac{\eta}{(\triangle - s)\, g} \cdot \frac{h}{t}};$$

all quantities measured in units of the c. g. s.-system.

6. *Experimental Arrangements.* — A sensitive balance was adapted to the purpose. In Fig. 1 A is a testing vessel of 110 —120 cc. capacity, containing the colloid to be examined. It is placed on a tablet that is supported by three legs provided with screws to adjust the position of the vessel. The plate B is made

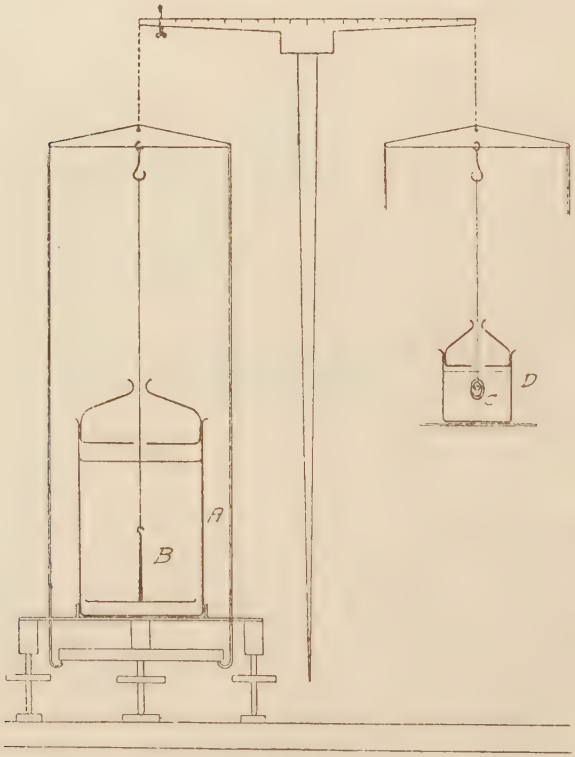

Fig. 1.

of copper. It is 42 mm. in diameter, 0,2 mm. thick and the edge is 0,55 mm. high inside. The plate is gilded and supported by a thin silver thread. To reduce the evaporation the vessel is covered with a lid that in the centre has a hole 2 mm. in diameter. The apparatus was placed in a cellar room where the temperature was tolerably constant. Since it varied within 0,5°, however, the variation of the specific gravity of the liquid (alcohol) had to be considered, the weighing plate having a volume of nearly 0,5 cc. So as to compensate the variations in question a piece of copper of the same weight as the weighing plate was hung, also in alcohol, from the other arm of the balance. This is necessary because, as we shall see presently, the weights to be determined were very small and the expansion of alcohol due to the heat is about 0,1 per cent per Celsius degree. The sensitiveness of the balance was so adjusted that 1 mg. corresponded to a movement of the pointer over 10 intervals of the dial, the vessels being filled with alcohol. The interval between two lines of the dial corresponds to a movement of the weighing plate of 0,06 mm. When the balance is in equilibrium the rider rests on the end of the left arm.

7. *The Colloids Registered.* — The vessel of the registering apparatus held about 120 cc. When the vessel was filled the volume of the liquid above the plate was about 70 cc. It is evident that in such a volume the colloid cannot hold much metal. Noble metals, on account of their instability, could not be produced in sufficient concentration to perform successive observations of weight. Following Svedberg, I used cadmium as a standard metal. The medium was ethylalcohol. The concentration of the sols was at most 0,2 g. per 100 cc. The dispersion could not be continued any further, since at a higher concentration the viscosity had increased in a few days to an enormous degree. I have not been able to produce colloids of sufficient concentration for the registering method of other metals than cadmium, bismuth and tin. After one or two weeks in suitable concentration the metal was generally oxidized by the decomposition products of the alcohol. As we cannot know exactly which particles are acted upon first the registering must be ended after a considerably shorter time. I have examined microscopically and analytically the sediment obtained after 30 hours. Within the

limits of analytical error the sediment was found to consist of globules of pure metal. The specific gravity and the viscosity of the colloids were examined in two cases. The colloids tested were a Cd sol and a Bi sol. They were examined after their sediment was registered. The specific gravity determined by a Westphal balance differed 0,1 per cent from that of pure alcohol. The viscosity was found to be 0,3 per cent lower than that of pure alcohol. Consequently we can state that in practice the specific gravity, s, and the viscosity, η, have the values of pure alcohol.

8. *Precautions.* — The sol should not be brought into the weighing vessel at once. It must first have acquired the temperature of the room. Before filling the vessel one should shake the colloid violently for several minutes. To prevent radiation of heat from outside the balance case is enclosed in a pasteboard box. The box is fitted with holes for moving the rider and observing the pointer. At the beginning of the operation series the accumulation of sediment is very rapid. It is therefore necessary to operate with the case uncovered. After ten minutes it is possible to place the box over the balance case without any hurry.

9. *Registering the Deposit.* — Before the beginning of the registration the balance was so adjusted that, the vessels filled with alcohol, it was in equilibrium at a deflection of the pointer of 5 lines to the left. Then the rider was removed and the arrestment placed in such a position that the pointer rested on line 6. Now the vessel A was emptied and filled very rapidly with the colloid, the time noted, and the vessel put back. Placing the rider some notches more to the right we can now observe the moment the pointer passes the equilibrium, at line 5 of the dial, note the corresponding weight, and remove the rider, the pointer then moving back to line 6. The operation is then repeated until the series of observations is finished.

10. *Maximum and Minimum Values of* **r**. — The minimum value of r is calculated directly according to Stokes' formula from the time t of the last observation. Since the observation series were concluded after 20—50 hours the minimum values of r are accordingly rated at 0,2—0,15 μ.

The maximum value cannot be calculated from the registering of sediment but must be determined by microscopical examinations. On emptying the dispersion vessel there will always be a remainder at the bottom. This remainder, which I have called coarse sediment, was weighed apart and could afterwards be examined under the microscope. The 10 greatest globules found were measured. In this way I obtained the average maximum value of r. These values were found to be

For Cadmium 25 μ
» Bismuth 100 »
» Tin 10 »

Naturally no distinct limit of size can be drawn between the coarse sediment and the first fraction of sediment registered. Because of that these two portions are added together in my diagrams.

11. *Graphical Representation.* — In order to get a survey we must illustrate the distribution of particles with size by means of a diagram. As the sediment registered contained globules of very different orders of magnitude I followed Odén and instead of the radius as abscissa I used its natural logarithm. The signification of the ordinates may be seen from the following. Let $\triangle S$ signify the percentage of dispersed metal between the limits r_1 and r_2. The corresponding points on the axis are then $ln\, r_1$ and $ln\, r_2$. The space between them may be $\triangle ln\, r$. Onthis base there should be placed a rectangle of such a height that its area amounts to the value of $\triangle S$, i. e. its height must be $\frac{\triangle S}{\triangle ln\, r}$ The series of rectangles drawn in this way will give a comprehensive view of the distribution of particles with size.

12. *Distribution curve.* — Assume that the intervals between the values of $ln\, r$ corresponding to those of $\triangle S$ are small. Now the position and breadth of the rectangles depend upon the experimental conditions and are accordingly to a certain extent accidental. So we shall obtain a better representation of the distribution of particles by drawing a curve through the tops of the rectangles in such a way that the area bordered by the curve, the axis, and two ordinates is as great as that of the corresponding rectangle. The curve obtained in this way we shall call the distribution curve. Now the ordinates do not denote

$\frac{\triangle S}{\triangle ln\, r}$ any longer but $-\frac{d\,S}{d\,ln\,r}$. The minus sign must be put, as, according to the definition in section 5, S decreases with increasing values of r. The differential quotient $-\frac{d\,S}{d\,ln\,r}$ gives at any point the value of lim. $\frac{\triangle S}{\triangle ln\, r}$ for $\triangle ln\, r$ tending towards 0. Consequently we will call the ordinate $-\frac{d\,S}{d\,ln\,r}$ the distribution density of particles in the interval $d\,ln\,r$. By integrating the curve within two values of r we shall find the corresponding percentage of particles.

I have used a simpler way of drawing the curve e. g. in Fig. 2 c. The middle points of the top sides of the rectangles are connected into a distribution curve[1]. The approximation does not cause any error of such importance as that of the experimental and theoretical errors of the registering method.

13. *Errors.* — The theoretical errors originate from the circumstance that in equations (1) and (2) we have used the quantities $\frac{\triangle P}{\triangle t}$ instead of $\frac{dP}{d\,t}$ and $\frac{d^2P}{d\,t^2}$ as in the equations (1a) and (2b).

Odén endeavours to make allowance for this error by his graphical interpolation. In Fig. 3 a, which represents the distribution curve of the sediment Table V, I have introduced the corresponding curve of Odén in order to render a comparison possible.

Theoretically Odén's method might be more accurate. In practice, however, I think the method of calculation used by me serves its purpose as well. In fact I am inclined to think that the errors of observation are so great that one should be satisfied with the general character of the distribution curve being correct. The last fraction is calculated on the basis of the assumption that no more sediment will form. In the equation

$$S = t\left|\left(\frac{\triangle P}{\triangle t}\right)_1 - \left(\frac{\triangle P}{\triangle t}\right)_2\right| \qquad (2)$$

then

$$\left(\frac{\triangle P}{\triangle t}\right)_2 = 0.$$

[1] The Svedberg and K. Estrup, Koll Zeit **9**, 259 (1911).

Accordingly the ascertained weight of the last fraction is too great, how much it is not possible to decide.

14. *Data and results.* — The following tables contain registrations of O-sols of cadmium produced under different condi-

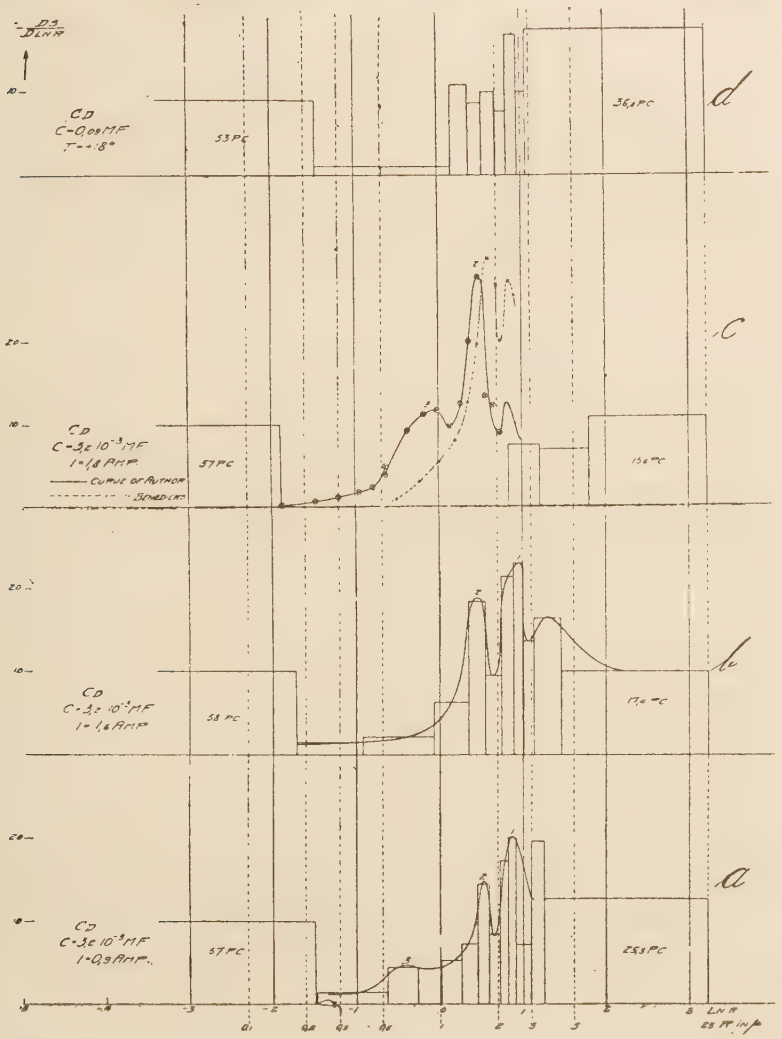

Fig. 2.

tions as to capacity, intensity, self-induction, temperature, and diameter of electrodes. The dispersion went on for 5 to 20 minutes. For such a long time it is impossible to keep the arc length accurately constant. I tis also self-evident that in this process

the arc length is indeterminate within certain limits. In fact the microscopical examination (see section 10) has shown that during the process globules are formed of about the same order of magnitude as that of the arc length. As at least part of these glo-

Fig. 3.

bules must have been between the electrodes it follows that during the process the arc length varies continuously. Where it is not otherwise stated the diameter of the electrodes was 5,6 mm. and the self-induction, leaving out of consideration the conducting wire of the oscillation circuit, was 0.

Symbols.

C Capacity
L Self-induction
A Length of arc
I Virtual current intensity
D Total weight of dispersed metal (= loss of weight of electrodes)
V Volume of sol registered
h Height of liquid above weighing plate
d Total weight in alcohol of dispersed metal above weighing plate
t Time
P Wight of esediment
T Temperature
R Weight of disperse phase in rest sol in per cent of D.

Table II. (Fig. 2, b).

$T = + 18°$.
$C = 3{,}2 \cdot 10^{-3}$ M. F.
$I = 1{,}6$ amp.
$A = 0{,}3 \pm 0\,1$ mm.
$D = 0{,}1907$ g.
$V = 110$ cc.
Coarse sedim. $0{,}0251$ g. $= 13{,}1$ p. c.
$h = 5{,}49$ cm.
$d = 0{,}1196$ g.

t			P
h.	m.	s.	mg.
	3	35	13
	4	30	15
	5	42	17
	6	59	19
	8	55	21
	11	23	23
	15	16	25
	22	37	27
	34	3	29
1	17	55	31
7	12		33
32	57		34
			= 28,4 p. c.

Temp. $= 15{,}0° \pm 0{,}2$.
$R = 58{,}5$ p. c.

Table III. (Fig. 2, a).

$T = + 18°$.
$C = 3{,}2 \cdot 10^{-3}$ M. F.
$I = 0{,}9$ amp.
$A = 0{,}3 \pm 0{,}1$ mm.
$D = 0{,}1686$ g.
$V = 110$ cc.
Coarse sedim. $0{,}0293$ g. $= 17{,}4$ p. c.
$h = 5{,}50$ cm.
$d = 0{,}1059$ g.

t			P
h.	m.	s.	mg.
	5	42	14
	7	44	16
	11	11	18
	13	24	19
	16	36	20
	21	33	21
	28	17	22
	41	36	23
1	7	22	24
2	2	—	25
4	10	—	26
22	55	—	27,1
			= 25,6 p. c.

Temp. $= 15{,}1° \pm 0{,}2°$.
$R = 57{,}0$ p. c.

Table IV. (Fig. 3, b).

$T = +18°$.
$C = 0{,}4 \cdot 10^{-3}$ M. F.
$I = 0{,}8$ amp.
$A = 0{,}3 \pm 0{,}1$ mm.
$D = 0{,}1526$ g.
$V = 110$ cc.
Coarse sedim. $0{,}0072$ g. $= 4{,}8$ p. c.
$h = 5{,}50$ cm.
$d = 0{,}0960$ g.

t			P
h.	m.	s.	mg.
	4	0	2
	9	35	4
	16	55	6
	23	0	7
	30	35	8
	42	15	9
1	1	45	10
1	40	45	11
3	3	15	12
5	1	—	13
8	15	—	13,7
25	—	—	14,9
			= 15,5
			p. c.

Temp. $= 14{,}5° \pm 0{,}3°$.
$R = 79{,}7$ p. c.

Table V. (Fig. 3, a).

$T = 18°$.
$C = 1{,}6 \cdot 10^{-3}$ M. F.
$I = 0{,}95$ amp.
$A = 0{,}3 \pm 0.1$ mm.
$D = 0{,}1656$ g.
$V = 110$ cc.
Coarse sedim. $0{,}0133$ g. $= 8{,}04$ p. c.
$h = 5{,}50$ cm.
$d = 0{,}104$ g.

t			P
h.	m.	s.	mg.
	1	51	5
	4	12	7
	5	25	8
	6	52	9
	8	28	10
	10	15	11
	12	32	12
	15	55	13
	19	51	14
	24	11	15
	31	25	16
	41	46	17
1	—	41	18
1	36	1	19
2	38	—	20
4	34	—	21
10	12	—	22
26	29	—	23
48	—	—	23,6
54	—	—	23,7
			= 22,8
			p. c.

Temp. $= 14{,}2° \pm 0{,}2°$.
$R = 69{,}2$ p. c.

Table VI. (Fig. 3, c.)

$T = -75°$.
$C = 0{,}4 \cdot 10^{-3}$ M. F.
$I = 1{,}0$ amp.
$A = 0{,}25 \pm 0{,}1$ mm.
$D = 0{,}1453$ g.
$V = 110$ ccm.
$h = 5{,}70$ cm.
$d = 0{,}0945$ g.
Coarse sedim. 0,0014 g. = 1,0 p. c.

t			P
h.	m.	s.	mg.
	11	30	6
	17	30	8
	27	—	10
	34	30	11
	50	—	12
1	16	—	13
1	48	—	14
3	28	—	16,4
5	58	—	18,0
21	30	—	18,3
			= 19,3
			p. c.

Temp. 17,8° ± 0,4°.
R = 79,3 p. c.

Table VII. (Fig. 3, b.)

$T = -75°$.
$C = 0{,}09$ M. F.
$I = 1{,}8$ amp.
$A < 0{,}05$ mm.
$D = 0{,}1030$ g.
$V = 104$ ccm.
$h = 5{,}90$ cm.
$d = 0{,}0764$ g.
Coarse sedim. 0,0209 g. = 20,1 p. c.

t		P
h.	m.	mg.
	9	13
	14	15
	18	16
	37	17
3	20	17,5
20	—	18,8
39	30	19,7
		= 25,8
		p. c.

Temp. 17,9° ± 0,4°.
R = 54,1 p. c.

Table VIII. (Fig. 2, d).

C = 0,09 M. F.
I = 1,1 amp.
A < 0,05 mm.
D = 0,1642 g.
V = 110 ccm.
h = 6,08 cm.
d = 0,114 g.
Coarse sedim. 0,0363 g. = 22,1 p. c.

t			P
h.	m.	s.	mg.
	9	—	20
	11	—	21
	14	30	22
	19	—	23
	25	—	24
	35	—	25
	53	—	26
4	45	—	27
23	—	—	27,8
			= 24,4
			p. c.

Temp. 18,0° ± 0,3°.
R = 53,5 p. c.

Table IX. (Fig. 4, a). Diam. of electrodes 2 mm.

C = $3{,}2 \cdot 10^{-3}$ M. F.
I = 1,3 amp.
A = 0,3 ± 0,1 mm.
D = 0,0870 g.
V = 105 ccm.
h = 5,30 cm.
d = 0,0552 mg.
Coarse sedim. 7,4 mg. = 8,5 p. c.

t			P
h.	m.	s.	mg.
	2	55	5
	3	38	6
	4	25	7
	5	24	8
	6	30	9
	8	—	10
	10	5	11
	12	57	12
	17	35	13
	23	40	14
	32	55	15
	50	10	16
1	35	—	17
5	2	—	18,1
21	20	—	19,1
			= 34,6
			p. c.

Temp. 15,3° ± 0,3°.
R = 56,9 p. c.

Table X. (Fig. 4, b).

$L = 2{,}000 \cdot 10^{-8}$ Henry
$C = 3{,}2 \cdot 10^{-3}$ M. F.
$I = 0{,}80$ amp.
$A = 0{,}20 \pm 0{,}05$ mm.
$D = 0{,}2003$ g.
$V = 105$ ccm.
$h = 5{,}35$ cm.
$d = 0{,}1270$ g.
Coarse sedim. 0,0114 g. = 5,4 p. c.

t			P
h.	m.	s.	mg.
	14	33	31
	19	20	33
	27	8	35
	43	40	37
1	48	—	39
6	32	—	40,4
21	7	—	41,3
45	7	—	42,0
			= 33,1
			p. c.

Temp. $15{,}4° \pm 0{,}3°$.
R = 61,2 p. c.

Table XI. (Fig. 4, c).

Bi
$C = 3{,}2 \cdot 10^{-3}$ M. F.
$I = 1{,}40$ amp.
$A = 0{,}3 \pm 0{,}1$ mm.
$D = 0{,}1018$ g.
$V = 110$ ccm.
$h = 5{,}58$ cm.
$d = 0{,}0614$ g.
Coarse sedim. 0.0272 g. = 26,7 p. c.

t			P
h.	m.	s.	mg.
	2	15	8
	3	4	9
	4	22	10
	6	15	11
	9	10	12
	12	52	13
	17	35	14
	25	—	15
	36	25	16
	55	35	17
1	47	—	18
4	50	—	19
22	50	—	< 20
			= 32,6
			p. c.

Temp. $17{,}5° \pm 0{,}3°$.
R = 40,7 p. c.

Table XII. (Fig. 4, d).

Sn

$C = 3{,}2 \cdot 10^{-3}$ M. F.
$I = 1{,}45$ amp.
$A = 0{,}20 \pm 0{,}1$ mm.
$D = 0{,}2066$ g.
$V = 110$ ccm.
$h = 5{,}52$ cm.
$d = 0{,}1280$ g.
Coarse sedim. $0{,}0352$ g. $= 17{,}0$ p. c.

t			P
h.	m.	s.	mg.
	3	0	14
	3	42	16
	4	28	18
	5	23	20
	6	28	22
	7	48	24
	9	30	26
	11	38	28
	14	28	30
	17	53	32
	22	41	34
	29	58	36
	39	22	38
	53	55	40
1	19	49	42
2	16	30	44
3	44	—	46
6	11	—	48
10	1	—	48,9
32	16	—	50,9
			= 39,8
			p. c.

Temp. $15{,}9° \pm 0{,}3°$.
$R = 43{,}2$ p. c.

15. *Calculation of Sedimenting Portion from Microscopical Measurements.* —

It is worth while to compare the results of the registering method with those obtained by some other method of observation. Accordingly I have counted and measured under the microscope all particles visible on a surface of known extension. From the statistics obtained I calculated the weight of the particles.

The material of observation was obtained by the following method of procedure. After stirring the sol violently 2 cc. was poured into a test tube, shaken with a drop of collodium and then poured out on a clean horizontal glass plate, the surface of which was 108 cm^2. The plate rested on an exactly level glass base until it was dry. The brown coloured film on the glass appeared even and uniform, except near the edges. Immediately after taking off the 2 ccm. for the plate I poured out the sol to prevent further accumulation of sediment. The coarse sediment was determined to be 15,6 per cent of the total weight of dispersed metal.

The eye piece was provided with a glass scale and a suitable diaphragm to border the field of view. The plate was fixed to the stage and 20 successive fields, 0,05 mm. distant from one another, were scrutinised. Then the plate was moved some millimeters and the observations repeated in the new place. The data are given below and in Table XIII.

Dispersed Metal: Cadmium.
$C = 3{,}2 \cdot 10^{-3}$ M. F.
I = 1,8 amp.
A = 0,27 mm.
Volume: 50 ccm.
Total weight of dispersed Cd: 88,5 mg.
Total concentration 1,77 mg./cm^3
Volume poured out on the plate: 2 cc.
Surface of the plate: 108 cm^2
Weight pr cm^2 : $3{,}28 \cdot 10^{-2}$ mg.

Microscope : 2 Leitz Wetzler, Jena.
Objective : 1/12 mm. Oelimm. N. A. 1 3
Eye piece : Ocular N°4.
Magnification : 1,000 x

Eye piece scale : 1 interval corresponds to 1,52 μ on the object.
Diaphragm : Diam. 20,9 interv.
Field of view : 79,6 μ^2

Estimating the systematic errors (in evaluating the eye piece scale and measuring the surface of the field of view) at 5 per cent and assuming that the accidental errors in measuring the particles neutralize each other we find the error of the total weight to be about 15 per cent. Thus the weight of the particles within the limits

$$0{,}1\mu < r < \infty \text{ is } 43{,}3 \mp 6 \text{ p. c.}$$
$$\text{at } I = 1{,}8 \text{ amp., } A = 0{,}3 \text{ mm. } C = 3.2 \cdot 10^{-3} \text{ M F,}$$

whilst according to the registering method the total weight of particles within the limits

$$0{,}18\ \mu < r < \infty \text{ is } 41{,}6 \text{ p. c.}$$
$$\text{at } I = 1{,}6 \text{ amp., } A = 0{,}3 \text{ mm. } C = 3{,}2 \cdot 10^{-3} \text{ M F.}$$

The agreement is sufficient.

The result is represented in Fig. 2c, where in arbitrary units a curve calculated from the measurements of Benedicks[1] is also introduced. The units of the ordinates must be arbitrary since Benedicks has not stated the total weight of dispersed metal in the colloid examined. We see, however, that the general shape of the two curves is the same.

16. *Discussion of Results.* — In equation (2) the accuracy of determination depends upon that of $\left(\frac{\triangle P}{\triangle t} - \frac{\triangle P}{\triangle t}\right)$. As long as this difference remains small the relative error of our determination will be enormous. After 5 to 10 minutes the difference in question has become so great that the error is not excessive. Consequently we shall direct our attention to the course of the curve for $r < 3\ \mu$ alone.

Let us examine the curves Fig. 1 a—c, which show the distribution curves of sols produced under similar conditions except for the current intensity.

[1] l. c.

Table XIII. (Fig. 2, c).

Diam. of particles in intervals of eye piece scale	Radius of particles	Weight of one particle in 10^{-9} mg.	Number of particles	Total weights of particles measured	Same w:s $\triangle$ S as a percentage of total weight of dispersed metal	ln r	$\triangle$ ln r	$\frac{\triangle S}{\triangle \ln r}$
a) Number of examined fields 20 = 0,016 mm^2. Total weight of dispersed metal 0,0522 . 10^{-4} mg.								
< 0,2	0,10	1,036	167	6,0	0,115	— 2,30	0,42	
0,2	0,15	0,127	45	5,7	0,110	— 1,88	0,40	
[0,3	0 23	0,430	24	10,3	0,198]	— 1,48		
					0,225			
b) Number of examined fields 200 = 0,159 mm^2. Total weight of dispersed metal 0,522 . 10^{-4} mg.								
[0,2	0,15	0,127	492	62,4	0,120]	— 1,88	0,40	0.24
0,3	0,23	0,430	287	123	0 236	— 1,48	0,28	0,71
0,4	0,30	1,01	168	170	0,307	— 1,20	0,24	1,22
0,5	0,38	1,99	102	203	0,389	— 0,96	0,17	1.94
0,6	0,456	3,42	60	205	0,393	— 0,79	0,15	2,4
[0,7	0,53	5,46	69	376	0,720]	— 0,63		5,0
					2,145			
c) Number of examined fields 705 = 0,560 mm^2. Total weight of dispersed metal 1,84 . 10^{-4} mg.								
0,6—0,8	0,53	5,46	401	2,190	1,19	— 0,494	0,30	4,0
0,8—1,0	0,68	11,8	322	3,780	2,05	— 0.274	0,22	9,3
1,0 1,2	0,83	21,1	177	3,740	2,03	— 0,094	0,18	11,2
1,2—1,4	0,99	34,9	95	3,310	1,80	+ 0,058	0,152	11,8
1,4—1,6	1,14	53,5	46	2,460	1,34	0,195	0,137	9,8
1,6—1,8	1,29	78	36	2,810	1,53	0,317	0,122	12,6
1,8—2,0	1,44	109	35	3 820	2,07	0,419	0,102	20,0
2,0—2,2	1,60	147	33	4,840	2,62	0,513	0,094	27,8
2,2—2,4	1,75	193	11	2,120	1,15	0,599	0,086	13,4
2,4—2,6	1,90	248	7 1/2	1,850	1,00	0,6805	0,081	12,3
2,6—2,8	2,05	312	4	1,250	0,68	0,756	0,076	9,0
2,8—3,0	2,20	387	4	1,550	0,84	0,825	0,069	12,3
3,0—3,2	2,35	471	2	942				
3,2—3,4	2,51	570	1	570				
3,9	2,96	940	1	940	2,78			
4,1	3,12	1,090	1	1,090			0,37	7,5
4,3	3,27	1,270	1 1/4	1,580		1,19		
4,9	3,72	1.870	1	1,870				
5,9	4,48	3,250	1/3	1,080			0,60	7,0
6,6	5,0	4,570	1/3	920	4,22			
7,9	6,0	7,800	1/2	3,900		1,79		
					25,30			

Summary.

Limits.		Percentage.
a)	$0,1 < r \leqq 0,2\ \mu$	0,225 p. c.
b)	$0,2 < r \leqq 0,6\ \mu$	2,145 » »
c)	$0,6 < r \leqq 6,0\ \mu$	25,30 » »
		27,7 p. c.
	Coarse Sediment	15,6 » »
	$0,10 < r < \infty$	43,3 p. c.

First consider the similarities. In fig. 1a—c I have numbered the maxima of the curves. Number 1 and 2 are rather conspicuous. In all three curves maximum number 1 is within $r = 2{,}3\ \mu$ and $r = 2{,}7\ \mu$ and maximum number 2 within $r = 1{,}6\ \mu$ and $r = 1{,}8\ \mu$. From $r = 1$ all the curves fall towards 0 as far as $r < 0{,}2\ \mu$, when the registering ceased. The maxima are of importance for estimating the accuracy of the registering method. In fact it is clear that the agreement of curves *a* and *b*, which were obtained by the registering method, with curve *c*, resulting from a statistical calculation, offers strong evidence of the applicability of the registering method. In comparison with these facts it seems to me that the variation of the heights of the maxima (especially of that of number 1) is of less importance. For according to the statistical measurements maximum 1 of curve *c* is calculated from only 4 globules. So it is natural that the percentage of these globules is rather uncertain. The shape of the curve obtained from Benedicks' measurements agrees better with my curves, perhaps owing to the fact that his statistics include a greater number of particles between the corresponding limit of r.

Finally it may be observed that the »rest sol» in all cases contains the same percentage, about 57 p. c., of dispersed metal.

The differences seem to be as follows. With increasing current intensity the coarse sediment decreases. At the same time the distribution density increases between $r = 1\ \mu$ and $r = 3\ \mu$, so that the total sediment remains constant.

Now if we look at all the curves, Fig. 2—4, we shall find the common characteristics to be these. The distribution density decreases from the maxima, which are between the limits $1\ \mu$ and $3\ \mu$. The weight of globules less than $1\ \mu$ in radius does not amount to more than about 5 per cent. From the tables we may also see that if we could continue the registration without disturbances for about 100 hours corresponding to $r = 0{,}1\ \mu$ only a slight quantity of sediment would settle to the bottom.

Moreover at the conclusion of the registration the globules have nearly reached the limit of microscopical visibility. Therefore the author feels inclined to agree with Benedicks when, assuming that the dispersed metal consists of melting globules, he writes[1]: »Diese haben überall den Eindruck gemacht überall

[1] Loc. cit.

aus so grossen Kügelchen aufgebaut zu sein, dass sie mit knapper Not durch das Mikroskop aufgelöst werden können und grösseren; aber selbstverständlich können auch weit kleinere Par-

Fig. 4.

tikeln vorkommen; *die Gesamtmasse derselben muss indessen ganz gering sein.*»

But if this proposition is correct what is the nature of the greater portion of dispersed metal, which does not sediment and

is not visible under the microscope? We shall return to this point in the next chapter.

17. *Total Sediment.* — With the above reservation concerning the very small melting globules we are entitled to consider the sediment obtained in about 30 hours as the total sedimenting portion. This portion we will call the total sediment. We shall also show later on that, if the sol is stable, the residue does not sediment at all, not even in a very long period.

Table XIV shows how the total sediment, S, and the weight, R, of metal in the rest sol vary under different experimental conditions. The sediment was determined in the following way: After about 30 hours the rest sol was cautiously poured out and the sediment washed down with alcohol into a crucible. The alcohol having evaporated and the contents dried, the residue was weighed as metal. As a test of the determination I have in several cases also determined the concentration of the rest sol. The determination was carried out on Cd-sols, the metal was determined as cadmium oxide. It appeared that within 3 p. c. the concentration agreed with that calculated from the weight of the sediment.

It appears from Table XIV that the percentage of total sediment is fairly independent of temperature, intensity, self-induction, and length of arc but increases with the capacity, at first rapidly, then slowly.

Table XV contains the total sediment S and the ratio R/S of different metals as well as some constants of the metals examined. It appears that R/S decreases in the main with the sinking of the melting point. Bismuth, however, presents a lower value of R/S than tin, though its melting point is higher, which seems to be due to its exceedingly low conductivity of heat. In fact it is most probable that the ends of Bi-electrodes melt to a greater extent than other metals, as the pulverisation of that metal gives rise to very large melting globules. Benedicks[1] has pointed out that other physical constants of the electrodes may also influence the quantity of dispersed metal.

[1] Loc. cit.

Table XIV.

Total sediment. Cd.

T	C MF	L Henry	A mm.	I amp.	S per cent	R per cent
+ 18°	$0{,}4 \cdot 10^{-3}$	0	0,30	0,75	20,4	79,6
— 75°	»	»	»	0,90	20,3	79,7
+ 18°	$1{,}6 \cdot 10^{-3}$	»	»	0,95	28,2	71,8
»	$3{,}2 \cdot 10^{-3}$	»	0,07	1,4	39,8	60,2
»	»	»	0,30	1,6	41,6	58,4
	»	»	0,62	1,5	42,8	57,2
»	»	»	0,30	0,9	43,0	57,0
— 75°	»	»	»	1,6	39,9	60,1
+ 18°	»	$2 \cdot 10^{-5}$	»	1,1	39,3	60,7
»	»	»	0,65	1,2	43,2	56,8
»	$12{,}8 \cdot 10^{-3}$	0	0,10	1,6	48,7	51,3
»	$90 \cdot 10^{-3}$	»	0,05	1,1	54	46

Table XV.

Total sediments of different metals.
$C = 3{,}2 \cdot 10^{-3}$ M. F. $L = 0$ $T = + 18°$.

Metal	A	I	S	R	R/S	Melt.-point	Boil.-point	Coeff. of heat conductivity
Pt	0,3	1,4	20,2	79,8	4,0	1,700	3.000	0,17
Au	0,3	1,6	25,8	74,2	2,9	1,064	2,500	0,7
Zn	0,25	1,7	41,0	59,0	1,44	419	918	0,26
Cd	0,3	1,6	41,6	58,4	1,40	320	780	0,22
Sn	0,2	1,4	56,8	43,2	0,76	232	2,200	0,14
Bi	0,3	1,4	59,3	40,7	0,69	268	1,420	0,016

CHAPTER III.

Pulverisation of Alloys and Analysis of Sediment.

18. *Preparatory Discussion.* — Concerning the sedimenting portion we have before emphasized the fact that the distribution density of particles decreases long before their size has attained the limit of visibility. In spite of this the main mass of metal remains in the liquid. Now assume the two groups to have different origins, e. g. the coarser portion being globules of split melted metal, the finer one being generated from gaseous metal condensing in the liquid. Then if we use electrodes of a suitable alloy the metal of lower boiling point will vaporize to a greater extent than the other metal. Naturally the total quantity of dispersed metal will have the same composition as the alloy. Consequently the two groups must have a different composition, the finer portion containing more, the coarser or sedimenting portion less of the metal of lower boiling point than the alloy itself. I have tested the above hypothesis on several alloys and am now going to give an account of my experiments.

19. *Producing the Alloys.* — For the gold alloys I used precipitated gold, since its melting point is high. The requisite metals were some grammes in weight, put into a crucible and warmed up to about red heat. To prevent oxidation some carbon was scattered upon the surface. The melted mass was stirred several times and, after about 20 minutes, the mass was poured into cylindric moulds of the desired diameter (about 6 mm.) The alloys obtained were apparently homogeneous and exceedingly hard.

Analysis.

The gold in the alloys was weighed as metal, the cadmium as oxide.

Au—Cd		
Au	Cd	Total
45,6 p. c.	54,2 p. c.	99,8 p. c.
45,6 »	— —	— —

Au—Sn
Au
42,6 p. c.
42,3 »

Further I made two alloys of cadmium and bismuth of different compositions. This time the moulds were bored out of a piece of oak.

1. 14 g. Bi and 5,9 g. Cd were melted together.

Analysis.

	Observ.	Calc.
Bi	71,0 p. c.	70,4 p. c.
Cd	29,6 »	29,6 »
	100,6 p. c.	100,0 p. c.

Table XVI.

m = weight of dispersed alloy.

All.	I	m g.	t	S g.	Analysis		Total
Au—Cd					Au 45,6 p. c.	Cd 54,2 p. c.	99,8
	1,6	0,1552	22^h	0,0565	» 65,5 »	» 34,5 »	100,0
	1,5	0,1425	20^h	0,0517	» 65,7 »	» — »	—
	1,6	0,3276	1) 4^m	0,0506	Au 63,2 »	Cd 36,4 »	99,6
			2) 20^h	0,0663	» 75,1 »	» — »	
Au—Sn					Au 42,5 p. c.	Sn 57,5 p. c.	—
	1,7	0,1541	24^h	0,0862	» 42,5 »	» — »	—
	1,6	0,1180	20^h	0,0692	» 43,3 »	» — »	—
	1,6	0,2850	1) 2^m	0,0786	» 43,2 »	» — »	
			2) 30^h	0,0759	» 44,7 »	» — »	
Bi—Cd					Bi 70 p. c.	Cd 30 p. c.	—
	1,0	0,1156	3^h	0,0507	» 77,3 »	» —	
Bi—Cd					Bi 50,5 p. c.	Cd 49,5 p. c.	
	1,3	0,1912	1) 2^m	0,0560	» 58 »	» 41 »	99
			2) 24^h	0,0231	» 66 »	» 34 »	100
	1,4	0,3931	1) $^1/_2{}^m$	0,1002	» 57,7 »	» 41,5 »	99,2
			2) 3^h	0,0441	» 62 »	» 36 »	98

2. The second alloy was produced by mixing 6,12 g. Bi and 5,99 g. Cd corresponding to the composition:

Bi	50,5 p. c.
Cd	49,5 »

The electrodes obtained were about as thick as the standard electrodes. The ends were made plane before using.

20. *Results and Conclusions.* — In Table XVI t signifies the length of time for which the colloid has been sedimenting, S weight of sediment.

Table XVII.

Ratio of components				Metals	Melt.-point	Boil.-point
Electrodes	Sediment		Rest sol			
Au/Cd						
0,84	1,9		0,52	Au	1,064	2,500
	First sed.	Second sed.				
	1,7	3,0	0,52	Cd	320	780
Au/Sn						
0,74	0,75		0,71	Au	1,064	2,500
	First sed.	Second sed.				
»	0,75	0,81	0,69	Sn	232	2,270
Bi/Cd						
2,3	3,4		1,8	Bi	268	1,420
1,0	1,5		0,77	Cd	320	80
	First sed.	Second sed.				
»	1,4	2,0	»			
[1]) Zn/Al						
1,5	—		2,17	Zn	430	950
				Al	657	1,800

[1]) According to M. Kutscherow's determination. Koll. Zeitschr. **11**. 165 (1912).

Let us examine Tab. XVII, where the ratios of the components are brought together. Regarding at first the total sediment in comparison with the alloy itself and the rest sol we see that in all cases the ratios are different, in some cases very different. This alone is not necessarily sufficient to prove a different origin for the two fractions. The composition might in some

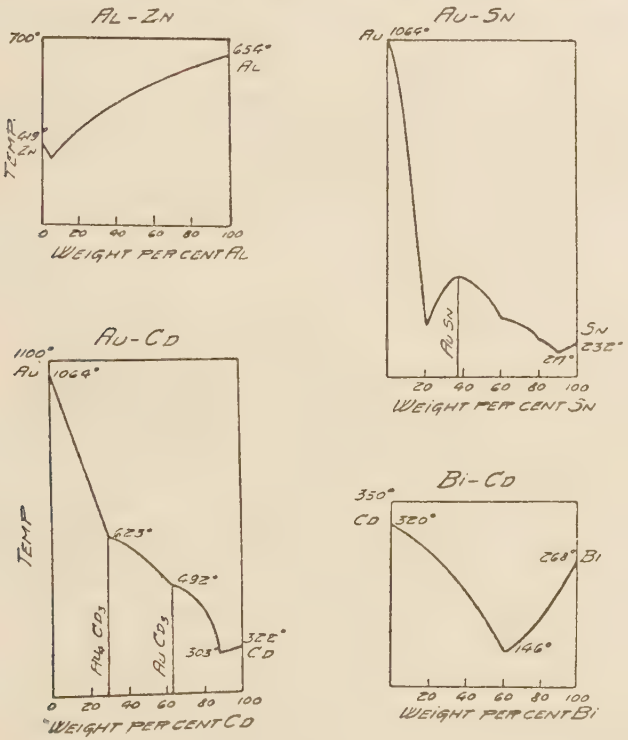

Fig. 5.

way be a function of the size of particles. But if we then regard successive fractions of the sediment their composition must continuously approach that of the rest sol.

Tab. XVII shows, however, that the ratios decidedly change in the opposite direction. This fact indicates very strongly the different origins of the two portions of dispersed metal.

Turning back to the character of the processes in question we cannot doubt the correctness of Benedicks' opinion that the sedimenting portion consists of globules in a melted state scattered in some way from the electrodes.

Regarding the finer portion let us consider the boiling points of the components of the alloys (see Tab. XVII). The sediments are always poorer in the more volatile metal, the rest sol accordingly richer than the alloy in the same metal. And further (we omit the alloy Zn—Al examined by Kutscherow, his statement not being complete) the difference between the composition of the fractions increases markedly with the difference between the boiling points. In fact, gold and tin have nearly the same boiling points and accordingly the sediment has nearly the same composition as that of the alloy. Again gold and cadmium have very different boiling points, 2 500° and 780°, and in consequence the ratios of the fractions differ considerably.

No connection can be found between the freezing-point diagrams of the alloys, Fig. 5, and the composition of the sediment. Consider again the successive sediments of melting globules (Benedicks' »Schmelzkugeln»). According to an argument of Benedicks[1] the composition of successive fractions should change in such a way that with diminishing size of particles the composition should follow the rising part of the freezing-point curve. This is the case with the alloys Au—Cd and Au—Sn but not with the second alloy Bi—Cd, the ratio of components of which is 1. Here the change is quite the opposite[2]. On the other hand in all cases examined the smaller particles are poorer in the more volatile metal than the coarser one. We shall return to this important point in discussing the mechanism of the electric synthesis of colloids.

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[1] C. Benedicks, Koll. Zeit. **11**, 263 (1912).

[2] The analytical results above completely reverse the arguments of Benedicks in his controversy with M. Kutscherow.

CHAPTER IV.

Colloids Produced by Means of Other Forms of Current.

21. *Synthesis of Colloids by Means of Wave Current.*[1] — In an article by The Svedberg[2] on »Wave-current Arc in Liquids» there are some remarks to be found on the dispersion of electrodes in the arc in question. We have carried out an investigation on this pulverisation in order to find out under which condi-

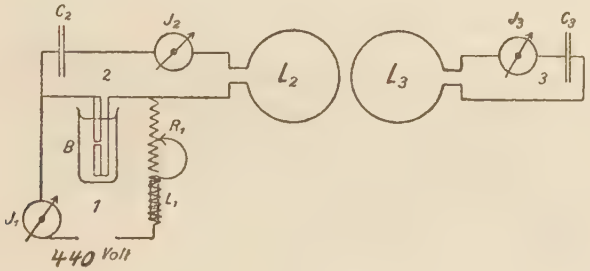

Fig. 6.

tions it gives the best result and in order to render possible a comparison with other methods.

The experimental arrangements are to be seen from Fig. 6. The arc B is burning in a vertical position in a vessel filled with liquid. Electrodes of the usual size are fixed in a Svedberg's micrometer. Explanation of the symbols in the figure:

Circuit 1:

L_1 Choking coil
R_1 Adjustable resistance
I_1 Continuous current ammeter

[1] In conjunction with Prof. The Svedberg the author has published the contents of this section in Koll. Zeit. **25**, 154 (1919). See also V. Kohlschütter, Zeit. f. Elektrochemie, **25**, 309 (1919).

[2] The Svedberg, Physik. Zeit. **15**, 362 (1914).

Circuit 2:

L_2 Coil of the self-induction $2 . 10^{-6}$ Henry
I_2 Hot-wire ammeter
C_2 Capacity

Circuit 3 is a resonator with an adjustable condenser with movable plates. It was used for determining the period of vibration of circuit 2. The energy for producing the wave-current was taken from the network of direct current of the town. The voltage amounted to 440 volts in all measurements. At this

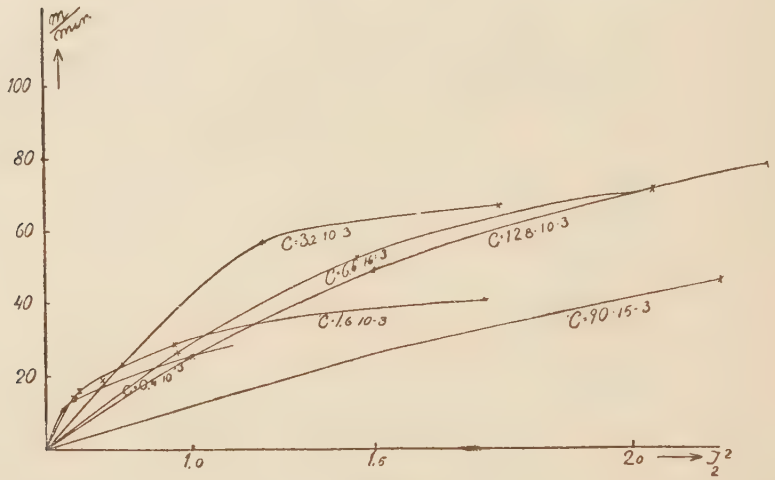

Fig. 7.

tension it is rather easy to keep the oscillations constant and accordingly the dispersion too. At 220 volts it is more difficult to obtain this constancy.

The current intensity I_1 was kept feeble and was never more than 0,5 amp. at contact of the electrodes. At great capacities it was even necessary to keep I_1 feebler than 0,1 amp. in order to prevent too great intensity of oscillations in circuit 2. The arc length must be small. Between cadmium electrodes in ethylalcohol the oscillations cease at an arc length of 0,06 mm. and between less dispersible electrodes at a still smaller arc length.

The influence of capacity and intensity on the pulverisation

and the decomposition of the medium[1] was first studied. The material of observation is presented in Tab. XVIII.

The symbols signify:

- n Period of oscillation
- I_c Intensity of the continuous current at contact of the electrodes
- I_1 Continuous current during the process
- I_2 Virtual alternating current of circuit 2
- m_a Loss of weight of the anode in mg.
- m_c » » » » » cathode » »
- m » » » » both the electrodes » »
- v Volume in cc. of gases produced
- t Temperature
- B Barometrical height in mm.
- v_o Volume of gases at 0° and 760 mm. (after subtracting pressure of dispersion medium)
- T Time of pulverisation in minutes.

At the determination of the pulverised quantity the time was always one minute and has not been introduced into the table.

The results of the observations are represented in the following diagrams Fig. 7 and 8. The independent variable is I_2.

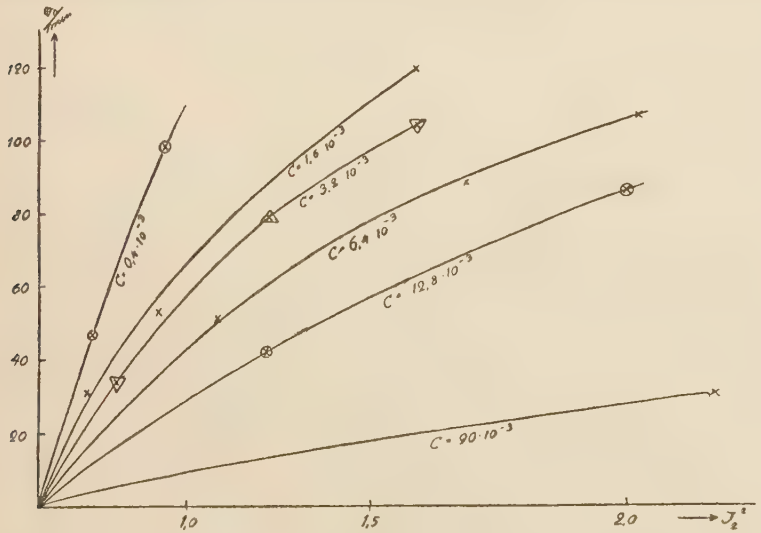

Fig. 8.

[1] As a measure of the decomposition the volume of gases formed at the dispersion was used. For reference see Svedberg, loc. cit. p. 33.

Table XVIII.

Length of arc. 0,05 mm.

Material of Electrodes Cd. Disperse medium Alcohol.

C . 10^3	n . 10^{-6}	Pulverisation					Decomposition of Medium						
		I_c	I_2	m_a	m_c	m	I_c	I_2	T	v	t	B	v_o
0,4	3,3	0,18	0,35	7,3	3,8	11,1	0,25	0,60	1	51,5	17,0	756	45,9
»	»	0,22	0,45	9,1	4,7	13,8	0,50	0,92	1/2	55,2	17,0	»	49,2
»	»	0,40	1,00	15,7	11,6	27,3							
1,6	1,95	0,20	0,47	11,4	5,2	16,6	0,30	0,90	1	62,0	16,0	»	54,9
»	»	0,22	0,62	13,2	5,7	18,9	0,50	1,60	1/2	67,2	16,0	»	59,6
»	»	0,30	0,94	19,1	9,5	28,6	0,20	0,55	1	35,0	16,5	»	31,4
»	»	0,50	1,75	22,8	14,7	40,5	—	—	—	—	—	—	—
3,2	1,06	0,22	0,72	18,8	8,2	27,0	0,20	0,72	1	38,0	17,5	»	33,8
»	»	0,32	1,20	29,7	25,9	55,6	0,32	1,25	1/2	44,4	17,5	»	39,5
»	»	0,50	1,75	36,1	29,9	66,0	0,50	1,60	1/2	58,2	17,0	»	51,9
6,4	0,75	0,20	0,95	17,5	9,2	26,7	0,21	1,10	1/2	29,2	18,0	»	25,8
»	»	0,30	1,46	32,3	20,1	52,4	0,32	1,70	1/2	50,0	17,5	»	44,4
»	»	0,50	2,03	40,2	30,7	70,9	0,50	2,05	1/2	60.8	18,0	»	53,8
12,8	0,47	0,25	1,50	31,0	18,1	49,1	0,18	1,24	1	47,5	18,0	»	42,0
»	»	0,40	2,25	44,2	34,4	78,6	0,40	2,00	1/2	49,0	18,0	»	43,3
90	–	0,15	2,15	33,7	13,0	46,7	0,15	2,15	1	32,5	17,5		28,9

Table XIX.

C . 10^3	Pulverisation			Decomposition of Medium					
	I_{eff}	T	m	I_{eff}	T	v	t	B	v_o
3,2	0,85	1	11,1	0,62	1	14,6	18	751	12,8
»	1,13	1	18,5	0,90	1	26,0	16	»	23,5
»	1,35	1	21,9	1,05	1	35,4	16	»	31,0
»	1,50	1	25,0	1,22	1	56,2	18	»	49,5
»	1,65	1	33,6						

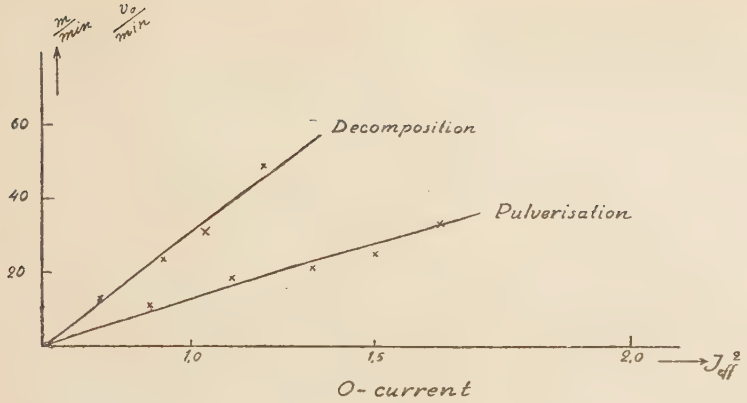

Fig. 9.

The diagrams resemble the corresponding ones obtained by The Svedberg[1]. The decomposition increases as in the case of Svedberg's oscillatory method at about the rate of the second power of the virtual current. With a feeble current the dispersion seems to have the same proportionality. With increasing intensity the dispersion curve turns off, afterwards increasing more slowly. The »knee» of the curve moves to the right with increasing capacity.

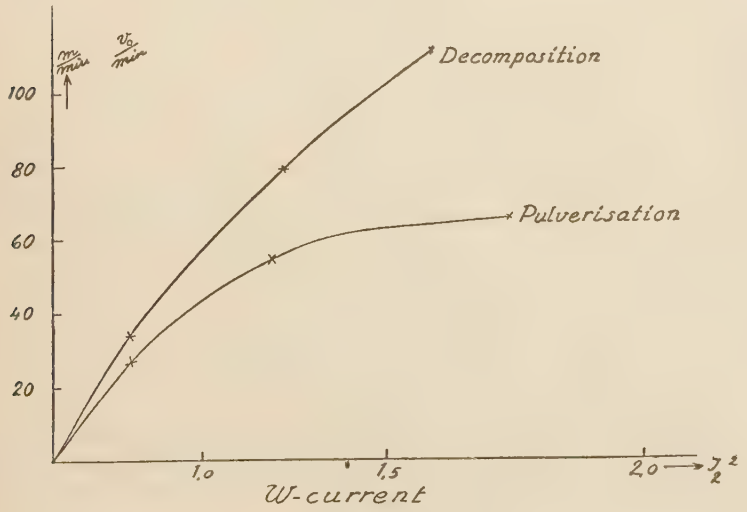

Fig. 10.

[1] Loc. cit.

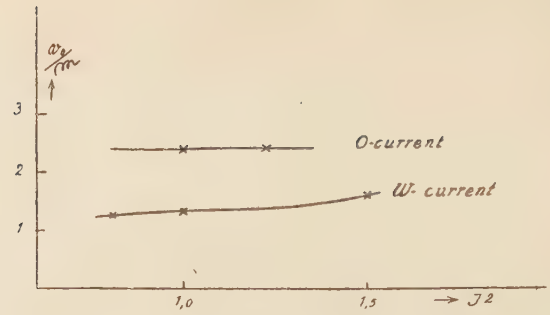

Fig. 11.

In order to get a comparison with Svedberg's oscillatory method we carried out some determinations by this method in the same dispersion medium. The results are to be found in Tab. XIX and the diagrams Fig. 9 and 10.

It appears from the diagrams that the pulverisation by the wave current method is much greater than the pulverisation by oscillating discharges. At 1 amp. the former is 3 times greater than the latter. The decomposition is in the former case twice as great as in the latter. Accordingly the »specific decomposition

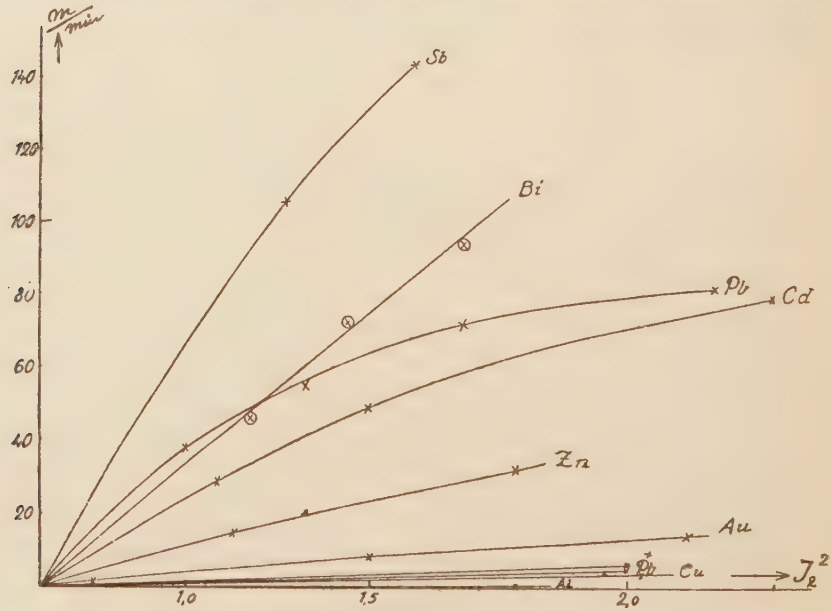

Fig. 12.

[1] The fourth curve from below represents Pt, the third Ag.

$\frac{v_o}{m}$ is less in the case of the new method. It increases some what with the current intensity. See Fig. 11.

Behaviour of different Metals.

The pulverisation was carried out at a capacity of $12{,}8 \cdot 10^{-3}$ M F. The results may be gathered from Tab. XX and Fig. 12. The decomposition was not determined.

With regard to the »cathodic hardness» of different metals the author would like to call attention to the following observations. The pulverisation per minute of the two methods is compared in Tab. XXI.

Now it is true that the wave current dispersion is carried out with a capacity of $12{,}8 \cdot 10^{-3}$ MF, while Svedberg used $3{,}2 \cdot 10^{-3}$ MF. But the capacity is not likely to affect the sequence of the elements. The greater capacity was chosen because then the pul-

Table XX.

Metal	I_c	I_2	T	m_a	m_c	m
Sb	0,25	1,30	1	64,4	41,2	105,6
»	0,30	1,60	1	85,4	58,2	143,6
Pb	0,15	1,00	1	18,6	19,6	38,2
»	0,20	1,35	1	25,7	29,8	55,5
»	0,27	1,70	1	33,4	38,9	72,3
»	0,40	2,15	2	75,8	87,6	163,4
Bi	0,20	1,20	2	58,9	33,8	92,7
»	0,25	1,45	1	45,7	27,2	72,9
»	0,30	1,70	1	54,7	38,9	93,6
Zn	0,15	1,15	2	21,2	7,9	29 1
»	0,20	1,35	2	30,3	11,3	41,6
»	0,25	1,80	2	47,5	17,2	64,7
Au	0,15	0,60	2	2,6	1,3	3,9
»	0,25	1,50	1	5,8	2,5	8,3
»	0,37	2,10	1	9,9	6,2	16,1
Pt	0,30	2,00	2	10,0	4,1	14,1
Ag	0,30	2,00	2	8,7	1,4	10,1
Cu	0,30	2,05	2	5,6	2,4	8,0
Al	0,30	1,80	2	0,1	0,3	0,4
Cd	0,25	1,50	1	31,0	18,1	49,4
»	0,40	2,23	1	44,2	34,4	78,6
»	0,18	1,10	1	18,0	10,7	28,7

verisation could more easily be kept constant. This was specially noticeable in using Bi and Pb. The use of a capacity of $3{,}2 \cdot 10^{-3}$ MF would increase the rate of dispersion about 30 p. c.

Tab. XXI shows some surprising differences between the two pulverisation methods. In order to fix our ideas we will divide the metals into cathodic soft and cathodic hard metals. The limit will be drawn between zinc and gold. Now it will be seen that the soft metals are dispersed much more easily in the wave current arc. The dispersion of antimony has increased more than five times, whilst the dispersion of lead has increased less than other soft metals. Consequently antimony and lead have changed places in the dispersion series. The pulverisation curve of lead turns off sharply as seen in Fig. 12. In Svedberg's series the pulverisation curve of bismuth has the same form.

In the case of the hard metals, on the other hand, the increase of the pulverisation is not very pronounced. In point of fact the rate of pulverisation, at least in one case, is even decreased, aluminium not being dispersed at all by the wave current arc. Now it is very striking that aluminium, especially in a melted state, exhibits a very high specific heat (0,4 cal.). The boiling point amounting to about 2 000°, the total heat of evaporation of aluminium will be 700—800 cal. This heat of evapora-

Table XXI.

$I = 1{,}5$ Amp.

Svedberg's method		Wave current method	
Metal	m. per minute	Metal	m. per minute
Pb	45 mg	Sb	130
Bi	33 »	Bi	75
Sb	25 »	Pb	64
Cd	21 »	Cd	48
Zn	8 »	Zn	25
Au	6 »	Au	10
Pt	3 »	Pt	4
Al	2 »	Ag	2,6
Ag	1,3 »	Cu	2,0
Cu	1,0 »	Al	0,1

tion is by far the highest that is to be found among the metals examined. The heat-conducting power is also considerable (0,35) and is surpassed only by Au, Ag, and Cu. It is not surprising that the facts mentioned above influence the dispersion in a different way in Svedberg's method. In fact, in this method the effective intensity during the discharge is of quite another order of magnitude than the hot-wire ammeter indicates. This would appear from the following discussion.

The oscillatory discharges are caused by about 140 breaks of the primary current. Assume that each break causes a discharges of the condensator, each discharge contains n oscillations and the number of vibration is 10^6. Then the current is in function

$$\frac{n\,a\,.\,140}{10^6} \text{ sec. per sec.}$$

Now let the hot-wire ammeter indicate 1 amp. The middle square of current intensity may then be calculated from the formula

$$I^2 \cdot \frac{n\,a\,.\,140}{10^6} = 1^2.$$

Consequently if $n = 10$, $a = 5$ (which may be considered to correspond to what is actually the case)

$$I^2 = \frac{10^6}{50\,.\,140} = \frac{10^6}{7\,.\,10^3} = 140.$$

The mean square of the intensity, and accordingly also the evolution of heat, is during the discharge at least 140 times greater in Svedberg's method than in the wave current method, the vibrations in the latter case being undamped and without interruptions.

Thus it is not improbable that the two methods have different effects on the electrodes.

A special action is shown by tin when pulverised by the wave current. On account of the high boiling point of this metal the electrodes have to be kept very near to one another, nearer than 0,01 mm., to excite the wave current. The melting point being very low the electrodes will easily be welded together, thus breaking off the process. It was therefore impossible to measure the rate of pulverisation of tin. Tin agrees with the hard metals

as to the length of arc. In fact the length of arc of hard metals has to be kept very small, not above 0,02 mm., while in the case of the soft ones it may be as much as 0,06 mm. before the wave current arc ceases.

22. *Consumption of Energy in Arc compared with Root-mean-square Value of Wave Current, I_2.* – As yet we have not taken into consideration the intensity I_1 of the primary current during the process. In order to be able to calculate the consumption of energy it is necessary to know this quantity together with the voltage. The latter is obtained from the formula

$$V = E\left(1 - \frac{I_1}{I_c}\right)$$

where E = 440 volt.

In Tab. XXII may be found the energy W (= $I_1 V$), produced by the primary current and further the quotient $\frac{I_2^2}{W}$.

It appears from the Table that except in the case of a very small length of arc (less than 0,016 mm.) $\frac{I_2^2}{W}$ is tolerably constant, i. e. the energy of oscillations is proportional to the energy produced by the primary continuous current. It may therefore be stated that the new method seems to be rather promising as it

Table XXII.

Material Cd. Disperse medium Alcohol.

A = arc length in mm. I_c = 0,30 Amp. C = $12{,}8 \cdot 10^{-3}$ M. F.

A	I_1	I_2	V	W	I_2^2/W
0,012	0,272	0,82	44	11,8	0,058
0,012	0,265	0,9	51	13,6	0,060
0,012	0,265	1,0	51	13,6	0,074
0,016	0,25	1,25	73	18,3	0,086
0,034	0,24	1,4	88	21,1	0,093
0,045	0,22	1,5	117	25,7	0,088
0,051	0,22	1,6	117	25,7	0,100
0,055	0,20	1,75	146	29,2	0,105
0,057	0,15	1,82	220	33,0	0,102
0,057	0,15	1,80	220	33,0	0,100

Table XXIII.

Material of electrodes Cd. Disperse Medium alcohol.
$C = 12{,}8 \cdot 10^{-3}$ M. F. $I_2 = 1{,}5$ amp. Time 1 minute.

A	I_c	I_1	V	W	m_a mg	m_c mg	m mg	m_a/m_c
0,025	0,50	0,43	55	2,4	40,4	18,2	58,6	2,22
0,029	0,45	0,37	64	2,4	40,2	16,8	57,0	2,39
0,032	0,40	0,33	74	2,4	39,1	17,0	56,1	2,30
0,033	0,35	0,28	85	2,4	36,0	15,9	51,9	2,26
0,040	0,30	0,23	100	2,3	33,9	15,9	49,8	2,13
0,050	0,25	0,15	175	2,6	29,6	18,6	48,2	1,59

makes it possible to obtain a relation of the rate of dispersion to the energy produced.

23. *Influence of Arc Length on the Rate of Dispersion.* — It is difficult to keep the length of arc constant even during such a short interval as 1 min., the pulverisation being rather intense and the length of arc small in relation to the threads of the micrometer. Consequently the ammeter also is rather unsteady during the process, so that the errors of observation

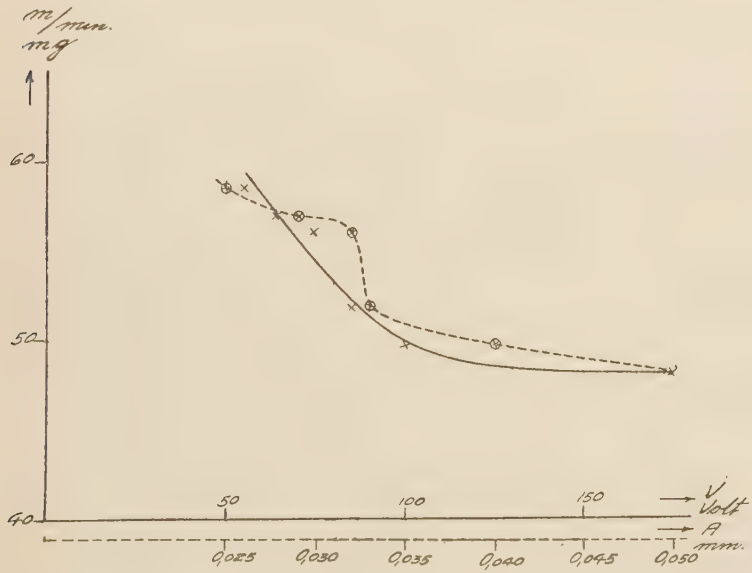

Fig. 13.

will be considerable. It appears, however, that the length of arc and the voltage correspond to one another and it is an obvious assumption that the voltage is about a linear function of the length of arc. This assumption seems to be verified to a certain extent by Fig. 13, where the rate of dispersion is indicated by the ordinate, the voltage and the length of arc respectively by the abscissa. From the curves it appears that the errors of observation of the length of arc are greater than those of the voltage. As a matter of fact it is impossible to estimate the length of arc with desirable accuracy, as the end surfaces of the electrodes do not remain exactly plane. Moreover, the base at which the upper electrode is fixed rocks when the space is regulated. From Table XXIII and Fig. 13 it will be seen that, at all events, *the rate of dispersion increases with decreasing length of arc and decreasing voltage respectively.* Accordingly the influence of the length of arc is the same in the new method as in Svedberg's oscillatory method.

24. *Influence of Temperature.* —

The disperse medium was stirred during the process. An attempt to make a determination in alcohol at −70° did not succeed, it being impossible to keep the process going without inter-

Table XXIV.

Material of electrodes Cd.

$C = 3{,}2 \cdot 10^{-3}$ M. F.

Medium	I_2	T	m/min. mg
Ether	1,8	− 100°	28,0
»	»	− 7,5°	27,6
»	»	+ 4°	27,6
»	»	+ 17°	24,0
»	»	+ 28°	16,7
»	»	+ 33°	15,5
»	»	Boiling.	11,0
»	»	Gas of	10,6
»	»	ether	8,0
Alcohol	0,8	+ 18°	33,0
»	»	+ 65°	17,3

ruptions. The results, referring to ether, are illustrated by Fig. 14. It appears that the rate of dispersion at a low temperature is constant up to about 0°. At a continued raising of the temperature, the rate of dispersion begins to decrease, first slowly, then more rapidly, until at boiling point it attains the same value as in gas of ether. The author wishes to draw attention to the fact that the rate of dispersion in gas of ether is about one third of that in the liquid at ordinary temperature. Experiences made up to this date have given rise to the assumption that the rate of dispersion in gases should be of quite another

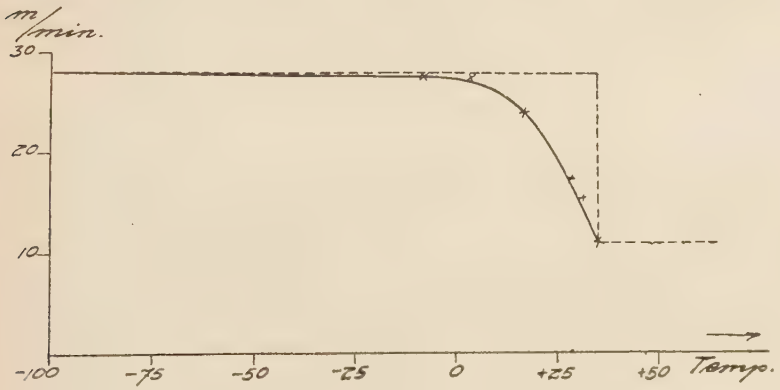

Fig. 14.

order of magnitude than in liquids. Table XXIV shows, however, that this is not always the case. Hence we must conclude that the rate of dispersion in gases depends on the nature of the gas.

The shape of the curve Fig. 14 gives rise to the conjecture that the influence of the medium is a double one. It might therefore be supposed that with perfect stirring the rate of dispersion in the liquid would be constant until the temperature had reached boiling point. At this point the rate of dispersion would suddenly fall to its value in gaseous ether (See Fig. 14). It may be added that in the vapour the vibrations are more regular, and that the length of arc can be made somewhat greater than in the liquid itself.

25. *Different Loss of Weight of Anode and Cathode.* — When using oscillatory discharges according to Svedberg's method no difference can be found between the two electrodes, both losing

the same quantity of metal. When using Bredig's method, in most cases only the cathode decreases in weight. On the other hand, observing the results in Table XX and XXIII, we see that the wave current has a different influence on the electrodes, the anode losing more in weight than the cathode. The curves Fig. 15 show the change of the ratio $\frac{m_a}{m_k}$ with voltage and length of arc, the dotted curve corresponding to the latter one. As in Fig. 13, the parallelism of the length of arc with the voltage is undeni-

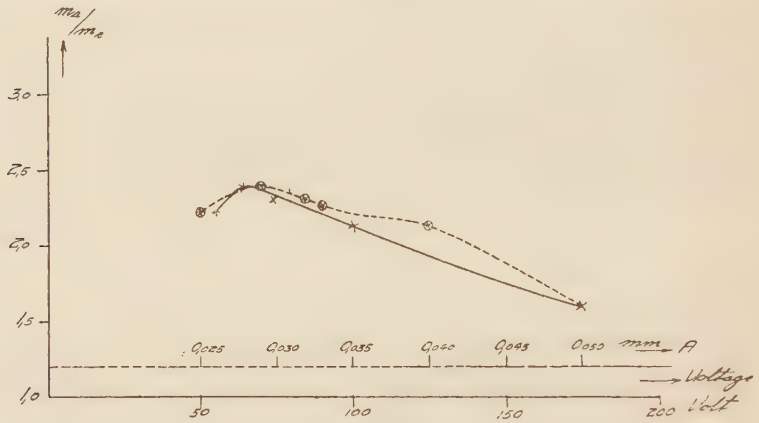

Fig. 15.

able. In fact, if we take into account the errors of observation of the length of arc, the two curves must be considered identical.

Previous results[1] had suggested that the ratio m_a/m_k was a function of the current intensity I_2. Later investigations on the subject have not indicated such a connection between the two quantities, so I must assume that the results mentioned were obtained because of the length of arc not being constant.

26. *Current Diagram.* — In the paper mentioned it was assumed that the wave current in the arc, according to the investigations of Blondel[2], never sinks below zero (Fig. 16a). Now Barkhausen[3] has stated that, under certain circumstances, »Rück-

[1] Koll. Z. **25**, 157, (1919).

[2] Blondel, Journ. de phys. (4), **5**, 79 (1906).

[3] Barkhausen, Jahrb. f. Drahtl. Telegr. u. Teleph. **1**, 243 (1907).

zündung» takes place, i. e. the current corresponds to the diagram in Fig. 16b. In fact, taking into account the high value of I_2 in comparison with that of I_1 (Table XXIII), and considering the fact that the vibrations in the oscillation circuit must be symmetrical, it is necessary to assume the wave current in the arc to be of alternating direction. Besides, Barkhausen states that in the case of »Rückzündung» the wave current is a very complicated one. Moreover, the appearance of the electrodes after the dispersion indicates that the current has been alternating, as no difference can be observed under the microscope between the anode and the cathode. Later we shall find a definite diffe-

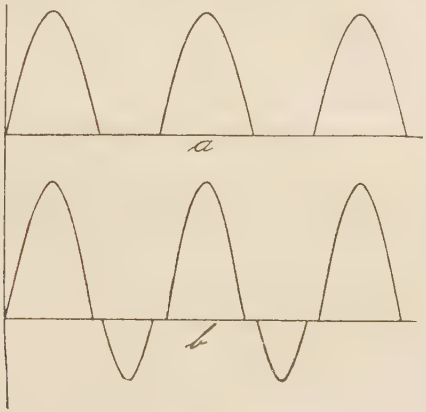

Fig. 16a, b.

rence between anode and cathode after the dispersion, when using a current of constant direction. So it seems natural to conjecture that the different loss of weight of anode and cathode is caused by the oscillations in the arc being unsymmetrical in intensity, though alternating in direction. Further we might perhaps be entitled to ascertain that the greater I_2 is in comparison with I_1, the more symmetrical will be the oscillations of the wave current. Consequently at a constant value of I_2 the ratio m_a/m_k should increase with I_1. The above discussion is supported by the results in Table XXIII.

27. *Sediment of Wave Current Sols.* — When metal is dispersed to a concentration sufficient to render possible a registration of sediment the alcosols do not remain stable. In

a few hours a considerable portion of the sol will have settled to the bottom as a black coagulum. So no registration could be carried out. However, alcosols of low concentration produce no coagulum, not even after a very long time. I was therefore able to calculate the sediment in another way. Instead of weighing the sediment I determined analytically the concentration of the sol after definite intervals. For that purpose 20 ccm. of the sol was evaporated, and the residue analysed.

Table XXV shows (1) that after 20 hours no more sediment settles to the bottom, (2) that the total sediment is somewhat smaller than that of sols gained by Svedberg's oscillatory method. The sediment was examined under the microscope. It consisted of metallic melting globules.

28. *Bredig Continuous Current Sols.* — When using Cd the electrodes were bars of the same diameter as before (5,6 mm.). The dispersion was carried out at the temperature of the room. The current was taken from the network of the town, potential difference 220 volt.

A = 0,15 mm.
I = 1,1 amp.
Loss of weight of electrodes 0,0760 g.
Coarse sediment 0,0024 »
= 3,2 per cent.

Table XXV.

T = Time after production.
Temp. = 70° d = Weight of disperse phase.
$C = 3{,}2 \cdot 10^{-3}$ M. F. S = Sediment in per cent.

Metal	I_2	Vol.	m mg	T hrs	Conc. mg/ccm	d mg	S p. c.
Cd	1,1	60	15,6	22	0,185	11,1	29
				120	0,175	10,5	33
Au	1,4	60	5,1	20	0,065	3,9	23,5
				168	0,065	3,9	23,5

The liquid was poured into the weighing vessel. After 24 hours the weight of the sediment was 0,2 mg. The experiment was repeated with the following result.

Coarse sediment 1,0 per cent.
Sediment on the weighing plate (20 hours) 1,0 » »

A third experiment gave 4,0 per cent coarse sediment, and after 24 hours no more sediment could be found.

Consequently, *when thick Cd-electrodes are employed scarcely any sedimenting globules reach the surrounding liquid.* The use of thin Cd-electrodes is impossible, because they fuse too rapidly. Gold electrodes, on the other hand, 0,5 mm. in diameter, give rise to a reddish sediment, consisting of microscopical melting globules. In addition to the sediment there are to be found a few macroscopical pieces that have fallen from the electrodes. No quantitative determination was made.

29. *Intermittent Current Sols.* — The fact that the continuous current produces no melting globules out of Cd-electrodes while a considerable quantity are obtained when using Svedberg's oscillatory method or the wave current method gives rise to the conjecture that it may perhaps be the interruptions that in some way cause the scattering of the melting globules. In order to test the tenability of this conjecture the conducting wire was coupled to the mercury-jet interrupter which was used in Svedberg's method together with the induction apparatus. Keeping the electrodes very near to one another the author succeeded in obtaining a Cd-alcosol of about the same appearance as in the sol obtained by Bredig's method. See Table XXVI.

Table XXVI.

N = Number of interruptions per second.
S = Sediment after t hours.
I_c = Intensity at contact of electrodes.

I_c	N	m_a mg	m_c mg	m mg	m_a/m_c	t hrs	S p. c.
1,4	120	8,3	18,2	26,5	0,46	4	37,0
1,7	140	10,0	18,0	28,0	0,56	3	36,8
1,9	160	11,6	23,4	34,6	0,50	3	36,0
1,3	1	— 27,0	+ 56,4	29,4	— 0,48	16	16,7

At the last experiment (Table XXVI) an ordinary quick-break turning switch was employed instead of the interrupter. The results not only go to show that the scattering out of melting globules is caused by the interruptions, but also that when the interruptions are rare the quantity of melting globules will be smaller. It is striking, however, that though the number of interruptions per sec. has sunk from 140 to 1, the sediment has sunk from 37 to 17 per cent only. The following may be a satisfactory explanation of this fact. It is evident that when the current is acting the volume of melted metal of the electrodes will in the beginning increase with time. Accordingly, when the current is

Fig. 17.

interrupted once per second the quantity of melted metal will depend upon the rate at which the sphere of melted metal increases. The result of the last experiments indicates that the sphere of melted metal increases very rapidly during the first second. Moreover it may be supposed that when the volume of melted metal is small the main part of it will freeze before being split. Finally it may very well occur that by itself it is more difficult to split a small sphere of metal than a large one. At any rate we must conclude that the small portion of sediment produced by Bredig's method is caused by a number of interruptions, which are inevitable when the dispersion continues for some minutes.

The anode and the cathode exhibit different aspects under a magnifying glass. The cathode, the surface of which has a me-

tallic brightness, is covered with round knobs bordered by minute waves, see Fig. 17. The anode is covered with a gray layer, probably caused by cataphoresis, Cd-particles being negative, and the marks of the electric arc are cavities of somewhat irregular form, see Fig. 17.

30. *Alternating Current* — In using an alternating current the length of arc must be kept very small. Only cadmium electrodes were pulverised. The process was rather irregular. The sediment appeared to contain a small quantity of coagulum.

I used an alternating current of three different periods of vibration.

A) Period 50 vibrations per second.

I_{eff} about 2,5 amp. V 130 volt. 1) Sediment after 15 minutes 38,0 %
» » 18 hours 49,6 %
2) Sediment after 4 minutes 42,3 %
» » 18 hours 52,2 %

B) Period 500 vibrations per second.

I_{eff} 0,5—0,6 amp. V 220 volt. Sediment after 15 hours 51,5 %

C) Period 1,000 vibrations per second.

I_{eff} 0,6 amp. V 200 volt. Sediment after 21 hours 44 %
I_{eff} 0,85 amp. V 320 volt. Sediment after 4 hours 45 %.

On the electrodes there could be observed both anodical and cathodical marks of similar appearance to those described in the preceeding section.

31. *Continuous Current with the Arc confined in a Quartz Tube.* — The dispersion apparatus was that devised by Svedberg[1] No magnetic field was employed. When using electrodes of gold the experimenter obtained, besides the sol proper, a sediment of microscopical particles. The sediment had not been weighed, but its quantity seemed to be considerable in comparison with the weight of the disperse phase of the sol.

32. *Summary.* —

1) The electric arc between metallic electrodes surrounded by a liquid generally produces two different portions of disperse

[1] Med. fr. K. Vet. Akad. Nobelinst. 5, N:r 10, sid. 7, Fig. 5 (1919).

metal, a sedimenting portion of microscopical, or nearly microscopical melting globules and the residue, which does not settle to the bottom unless it coagulates.

2) The two portions are products of different processes. That is evident from the analysis of pulverised alloys.

3) The sedimenting portion is formed by melting metal being split and scattered into the surrounding liquid.

4) The scattering power is caused, in most cases, by interruptions of current. When electrodes of Cd, 5,6 mm. in diameter, are used and the length of arc is kept small the continuous current arc burns rather calmly and so no melting globules reach the surrounding liquid. When using thin electrodes of gold the continuous current arc too gives rise to melting globules in the liquid.

5) With Svedberg's continuous current method with the arc confined in a quartz tube the melting globules are blown out by the nitrogen current through the hole of the tube.

6) The particles of the »rest sol» are produced by condensation of metallic gas.

Part II.

Sols Proper.

CHAPTER V.

Properties of Electric Sols.

33. *Stability.* — As we are not at present considering the size of particles, we cannot employ the word stability in a very definite sense. So we shall characterise those sols as stable that are not subject to any visible change of appearance or concentration. In so doing we will leave out of consideration the chemical changes of the disperse phase.

General observations on the stability of isobuthyl-alcosols have been published by Svedberg[1]. Here we shall study the stability of ethyl-alcosols. My experiments go to show that several metals can be obtained as stable sols when a high concentration is not required. Table XXVII contains the concentration of some stable and unstable sols. Among the stable sols I have chosen the strongest ones, but it is not suggested that they represent the maximum limits of the concentration.

In no case were unstable O-sols of Zn or Cd obtained, nor stable sols of Al, Sb, Cu, Hg or Ag, while O-sols of other metals are sometimes stable, sometimes not. Electric sols often coagulate without any discernible cause. The author has occasionally produced a series of a very great number of Au-alcosols without succeeding in obtaining any stable ones. As the disperse phase of Au-sols is not subject to any chemical change the observations regarding their stability could be extended infinitely. I have preserved an Au-alcosol for more than a year and have ascertained that the concentration had not changed. No systematic examination has been made to find the conditions of obtaining stable Au-alcosols. However, as the result of a fairly wide experience I venture to formulate the conditions as follows.

[1] l. c. p. 84.

Table XXVII.

O-sols.

C = concentration in mg per ccm.

Stable sols		Unstable sols		
Metal	C	Metal	C	Coagulated in
Zn	0,7	Al	0,21	1 hour.
Cd	2,5	Sb	0,20	1 minute.
Fe	0,13	Cu	0,12	30 minutes.
Sn	2,0	Hg	[1]) 1,0	2 hours.
Bi	2,0	Ag	0,15	4 »
Pt	0,5	Sn	1,3	1 day.
Au	0,8	Bi	0,85	3 days.
		Pt	0,30	7 »
		Au	0,25	3 »
		»	0,25	1 hour.

Stable Au-alcosols are best obtained by O-current at

Small capacity
Feeble intensity
Low temperature
Low concentration.

When a stable sol is obtained it can be concentrated very far by evaporation. The stability seems to increase with time. An Au-alcosol that had been preserved for some months was kept boiling 10 hours without coagulating. Afterwards it was apparently unchanged. Even when the sol was evaporated to dryness in a crucible it did not seem to coagulate. The gold covered the walls as a thin dark red layer which was nearly black on the bottom of the crucible. If the crucible is heated to redness in order to remove the organic decomposition products, the layer alters into light red and the bottom is gilded. The heating of a coagulated residue has not the same effect, no uniform layer being formed, nor does the coagulum alter its dark blue colour.

Because of the meaning we have given the word stable in the present section we have also to consider the case when the

[1]) The sol contained a considerable quantity of large particles.

concentration changes without coagulating, i. e. when the disperse phase settles to the bottom in the course of time.

From the above we may draw the conclusion that such a change of concentration can not at any rate be observed unless a very long time is taken into consideration. Again, gold alcosols are for this reason the fittest objects of examination. Generally speaking, stable alcosols of metal do not change their concentration in the course of about two weeks. In the case of Cd and Zn the observations cannot be continued for a longer time, the alcosols being destroyed by chemical processes after that time. Bi- and Sn-sols are constant at least for one month, Pt- for 6 months and Au-sols practically infinitely. The alcosols of Au and Pt do not lose their stability when diluted with water. Because of this I was able to make the following experiment. Using the nuclear method of Zsigmondy as modified by Doerinckel[1] I prepared a gold hydrosol of about the dispersity $r = 20\,\mu\mu$. I poured 25 ccm. of the hydrosol into one beaker, and 25 ccm. water in another. Then I mixed 1 ccm. alcohol with the hydrosol and 1 ccm. of a strong gold alcosol with the water. The two hydrosols obtained contained about the same quantity of gold (0,8 mg.). The beakers were covered and put side by side in the cellar. After 5 days a slight sediment had settled to the bottom in the hydrosol of $r = 20\,\mu\mu$ and the upper part of the liquid exhibited, some millimeters under the surface, a not very distinct limit between the particles and the clear liquid. In the other beaker, containing the diluted alcosol, not the slightest change could be observed. The above experiment goes to show that the particles of the electric alcosols are either exceedingly small or of quite another specific gravity than ordinary metal particles.

What has been said above concerning O-sols is also applicable to W-sols. But they are not to be had in such concentration as O-sols. W-sols of Cd often coagulate when produced in a concentration of more than 1 mg. per ccm. A stable Au-alcosol, some months old, contained 0,25 mg. per ccm. Sols obtained by other forms of current have not been studied very closely by the author. Bredig's method gives stable Cd-alcosols, but stable

[1] F. Doerinckel, Zeitschr. f. anorg. Chem. **63**, 344 (1909).

sols of Au could not be obtained either in alcohol or in pure water.

S-sols of Ag and Au in alcohol are stable.

34. *Notes on alcogels of Cd.* — If an O-sol of Cd containing 0,2 g per 100 ccm. is preserved for some days, the sol grows gelatinous without coagulating. The consistency of the gel is loose, stirring destroys the gel and makes the mass liquid like ordinary alcohol. After stirring the disperse phase forms a loose coagulum. A sol containing 0,5—0,6 g Cd per 100 ccm. grew gelatinous in 2 days. After 4 days the mass was white without having lost its gelatinous structure.

35. *Absorption of Light. Tyndall Effect.* — As a rule the power of absorption of light of electric sols is not constant. It changes rapidly in the beginning, then at a slower rate. The measurements were carried out by means of a König-Martens' spectral photometer. As a source of light a mercury-vapour lamp of quartz glass was used.

Symbols:

λ = length of wave

$$k = \frac{1}{d \log e} . \log \frac{I_1}{I_2} = \text{absorption coefficient}$$

where

d = Thickness of layer in cm.

I_1 = intensity of light after passing through the pure disperse medium

I_2 = intensity of light after passing through the alcqsol.

All values of k are reduced to a concentration of 1 mg. per 100 ccm.

The changes of the Cd-alcosols are illustrated by Table XXVIII and Fig. 18.

Curves I a and I b indicate that when the metal is dispersed only to a low concentration the temperature of the disperse medium has no great influence upon the absorption of light. Curves II a and II b are also rather similar to each other. Still there is a difference, the cause of which will be seen from the following. Curves III, IV and V represent one and the same sol at different points of time, the first immediately after

Table XXVIII.

Absorption of Light of Cd-alcosols.

Curve Number	C	I	Temp.	Conc. mg per ccm.	k						Age of sol
					λ = 405 $\mu\mu$	436 $\mu\mu$	492 $\mu\mu$	546 $\mu\mu$	577/79 $\mu\mu$	623 $\mu\mu$	
				O-sols							
I a	$0{,}4 \cdot 10^{-3}$	0,7	— 75°	0,27	0,830	0,646	0,504	0,377	0,318	0,312	1—30^{m}
I b		0,6	+ 17°	0,26	0,800	0,617	0,484	0,354	0,303	0,276	»
II a	0,09	2,0	— 75°	1,20	0,782	0,667	0,582	0,484	0,433	0,399	10—40^{m}
II b	»	»	+ 17°	0,50	0,727	0,567	0,508	0,415	0,372	0,372	»
III	$3.2 \cdot 10^{-3}$	1,5	+ 17°	1,30	0,788	0,626	0,489	0,359	0,316	0,306	1—30^{m}
IV	»	1,6	+ 17°	1,57	0,450	0,386	0,386	0,292	0,266	0,240	6^{h}
V	»	»	+ 17°	»	0,149	0,096	0,057	0,035	0,034	0,030	30^{h}
VI	»	»	— 75°	0,78	0,595	0,534	0,511	0,398	0,361	0,356	16^{h}
				C-sol							
VII		1,0	— 75°	0,19	0,486	0,436	0,344	0,276	0,253	0,208	15 - 60^{m}

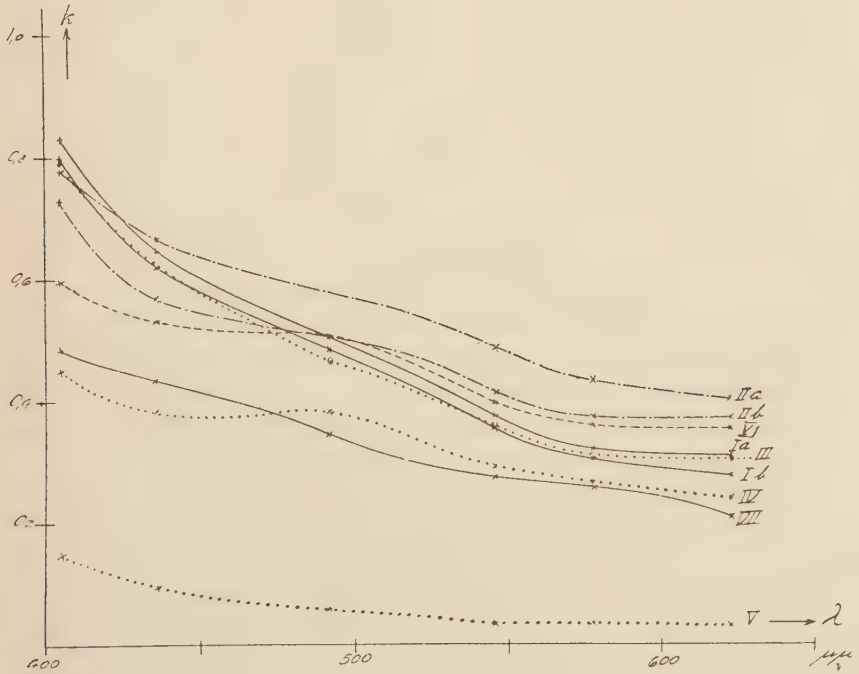

Fig. 18.

production, the second 6 hours, the third 30 hours afterwards. They prove that the absorption of light has decreased considerably in the course of time. On the other hand, when the dispersion is carried out at a low temperature the power of absorption of light decreases slowly. This is made evident by Curve VI (age of the sol 16 hours), which does not differ very much from curves II a and II b, representing fresh sols. Now it is an obvious assumption that the decrease of the absorption coefficient will be slower in a diluted sol than in a concentrated one. In fact such an assumption is supported by curves II a and II b. It appears from Table XXVIII that sols II are more concentrated than sols I. Accordingly the absorption coefficient of sol II b produced at + 17° must decrease more rapidly than that of sol I b produced at the same temperature. So the difference between curves II a and II b must be greater than that between I a and I b. See Fig. 17.

I have summed up my observations on the subject as follows.

The absorption coefficient of *fresh* sols is independent of temperature and intensity, it is but little changed with the increase of capacity. The colour of diluted sols is yellow, that of concentrated sols dark-brown.

The colour of a continuous current sol (curve VII) is similar to that of an old O-sol (curve IV).

The absorption of light of Au-alcosols changes very slowly, except perhaps during the first few seconds. In fact, at the first moment the sol presents an indefinite, dark-blue tint. Rather soon, however, it turns violet and remains so for several months. Very old sols have obtained a reddish colour. The results of the measurements are to be found in Table XXIX and are graphically represented in Fig. 19.

Comparing curve a (fresh sol) with curve b (old sol) we see that the absorption maximum moves with time in the direction of increasing length of wave. At the same time the absorption coefficient increases at the end of the short lengths of wave, but decreases considerably at the end of the red ones.

Curve d represents a fresh W-sol. It helps to show the similarity of W-sols to that of O-sols (Curve a). Under the conditions $T = 75°$, $C = 0{,}4 \cdot 10^{-3}$ M. F., $I_{eff} = 0{,}35$ amp., length of arc $< 0{,}02$ mm., the author obtained an O-sol that turned

Table XXIX.

Absorption of light of Au-alcosols.

Curve	Sol	k					
		$\lambda = 405 \mu\mu$	$\lambda = 436 \mu\mu$	$\lambda = 492 \mu\mu$	$\lambda = 546 \mu\mu$	$\lambda = 577\text{-}79 \mu\mu$	$\lambda = 623 \mu\mu$
a	O-sol + 17° Age 2 days	0,332	0,374	0,468	0,401	0,401	0,421
b	O-sol + 17° Age 14 months	0,423	0,335	0,412	0,460	0,405	0,231
c	O-sol — 70° Age 10 days	0,416	0,399	0,463	0,470	0,398	0,375
d	W-sol — 70° Age 10 days	0,285	0,379	0,456	0,380	0,372	0,339

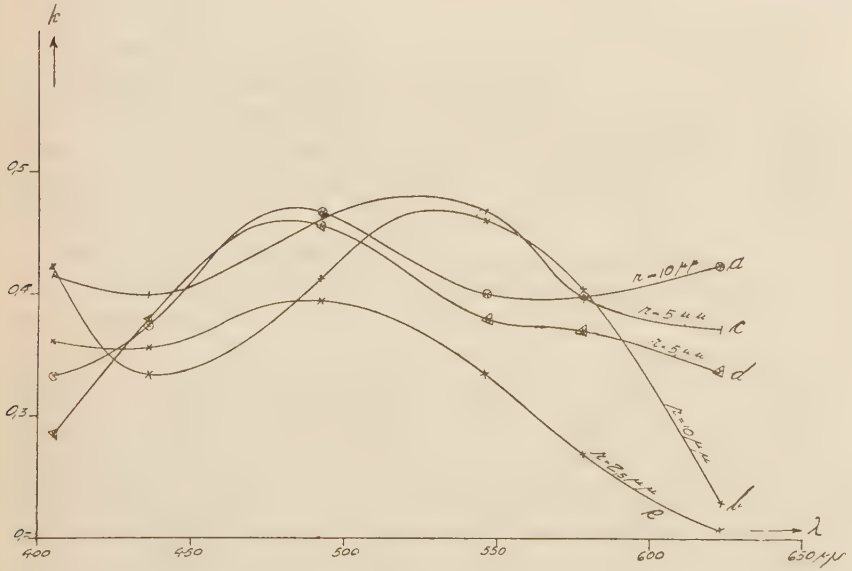

Fig. 19.

red at once. Its absorption diagram is shown in Fig. 19 c. In the figure there is also reproduced the absorption of an S-sol (Svedberg's method with the arc confined in a quartz tube) measured by Svedberg.[1] The absorption coefficients are reduced relatively to the proportion of silicic acid of the sol. See Fig. 19 e.

[1] Meddel. från K. Vet.-Akad:s Nobelinst. 5, N:o 10,16 (1919).

The author has made no measurements on the Tyndall effect of colloids. The following observations may, however, be of some interest.

The Tyndall effect of O-sols of Cd is, as a rule, very feeble. Diluted sols in ordinary daylight appear perfectly clear. Concentrated sols are almost black, especially when produced at $-75°$. In the course of time the Tyndall effect seems to increase. C-sols appear grey in incident light, as do old concentrated O-sols.

O-sols of Bi also present a feeble Tyndall effect. Even old sols are black in incident light. The lack of a strong Tyndall effect in O-sols of Bi is of some importance, because, in spite of this the particles are very large, as we shall see later. Occasionally I have observed the absence of any Tyndall effect in O-sols of Cd containing almost microscopical particles. A similar observation has also been made on a Cu-sol. See section 39, where a probable explanation is also suggested. O-sols of Sn appear grey in incident light, a strong Tyndall effect being thus indicated. As, however, the absorption of light is feeble, a comparison with other sols is not reliable. Finally it may be mentioned that, as a rule, Au-sols do not exhibit any Tyndall effect in ordinary light.

In diluted alcosols a ray of light from an arc lamp produces a bluish Tyndall cone.

36. *Chemical Changes. Degree of Purity.* — As is well known, an organic disperse medium is subject to decomposition during the pulverisation. As a measure of the decomposition the author, following Svedberg[1], has used the quantity of developing gas. It is, however, evident that part of the decomposition products, not being gaseous, remain in the liquid. The author has not attempted a determination of the products mentioned, but has only tried to find their weight in relation to the weight of the pulverised metal. After the evaporation of a Cd-alcosol to dryness the residue consists of a black or grey mass containing the metal and the decomposition products. The latter adhere exceedingly fast to the metal. It was not possible to wash them away, either by ether or by alcohol. The same thing is found by

[1] l. c. 33.

Degen[1], who has examined Pt- and Mg-alcosols in this respect. He has arrived at the opinion that the bulk of the decomposition products is free carbon. For my part I cannot confirm his statement, at least in the case of Cd- alcosols, on account of the following observations. The dry residue of a Cd-alcosol (O-current) containing 0,10 g. of metal was dissolved in diluted warm sulphuric acid. The weight of the oily and grey remains was 1,2 mg. If dissolved in hydrochloric acid too the substance does not leave any perceptible residue of free carbon. If free carbon were present in the substance, why should it not be visible when the metal is dissolved? Immediately after the production a Cd-sol is very dark. As is stated in section 34, the sol grows lighter in the course of time. This behaviour is at least partly due to a chemical change of the metal. An O-sol of Zn produced at the temperature of the room grows absolutely white in 4 hours. A Cd-sol requires a longer interval of time to undergo the same change. A very strong O-sol of Cd was produced, containing 0,3 g. in 60 ccm. alcohol. After 4 days the sol consisted of an absolutely white gelatinous mass. When evaporated to dryness, the mass formed a white powder, which was rapidly dissolved in diluted hydrochloric acid without developing gas. This action of the substance is difficult to explain if elementary carbon is assumed to be present in the liquid. The heating of the powder in a crucible gives rise to a reduction of the substance, which would appear from the fact that part of the metal volatilizes. Hence we must conclude that the white substance contains organic products. The disperse medium being alcohol, an obvious conjecture is that the substance partly consists of Cd-alcoholate. But there are other possibilities as well to take into consideration. The decomposition products might, for instance, be supposed to contain organic acids which together with Cd would form organic salts. In fact there is some probability in such an assumption. For an old Au-alcosol has a refreshing smell like that of ethylacetate, indicating that alcohol has combined with the acids to esters.

The decomposition products are subject to changes, which seems to be indicated by the fact that a new Au-alcosol has a curious unpleasant smell, while an old one, as we have men-

[1] Karl Degen, Inaug. Diss. Greifswald 1903.

tioned, has a pleasant smell. We cannot therefore be certain of arriving at the quantity of the decomposition products present in the liquid by determining the weight of the residue after evaporating to dryness. It is also impossible to determine how much belongs to the chemical combinations of the metal and how much consists of the decomposition products only. Moreover the weight of the residue is not constant, as is shown by the following determination.

A C-alcosol af Cd was evaporated to dryness on a water-bath. The weight of the residue was then

0,1188 g.

After two hours in a drying oven at 110° it was

0,1201 g.

and after 10 hours

0,1220 g.

The substance contained 0,1019 g. Cd (weighed as CdO) = 86 per cent. The residue of an O-sol of Cd shows a similar action, but contains only about 80 per cent Cd if the sediment is not counted.

It was of some interest to decide whether the decomposition products exist as solid particles to any considerable extent in the liquid or whether they are dissolved. For this purpose I produced an electric arc in the liquid between electrodes of carbon. The arc having been acting for 2 minutes, no colour or turbidity could be observed, whereas when metal electrodes are used under similar conditions the liquid presents an intense colour. According to Svedberg's[1] determination the rate of decomposition depends very little on the material of the electrodes. Consequently we must conclude from the experiment that, in all probability, no solid decomposition products are present in the liquid. In particular we are entitled to assume that the decomposition products do not affect the power of absorption of light as long as we keep in view the visible spectrum only.

As to the purity of the metallic particles Degen[2] has stated that in Mg-alcosols, obtained by Bredig's method, the particles consist of metal. In the case of Zn- and Cd- particles I venture to assert that at least the bulk of them are pure metal, as the Zn-particles dissolve in hydrochloric acid with a development of

[1] l. c. 64—66.

[2] l. c.

gas, and the Cd-particles behave in the same way, though the process is slower. In order to ascertain whether the particles contained any carbonate, I made the following experiment. The bulb of a small blow-pipe flask (see Fig. 20) was filled with strong hydrochloric acid. The dry substance of an evaporated Cd-sol, 0,07 g. in weight, was placed on a thin plate of platinum. The plate was then put into the upper part of the flask. After having connected the flask with a fine capillary tube, dipping into baryta water, I shook down the plate into the acid. At first a scarcely perceptible bubbling could be seen, then the production of gas became very slow. The baryta water was not made turbid. Now it is true that carbondioxide was produced when the flask was warmed. But the carbon dioxide must be held to originate from the organic substances, since cadmium carbonate is easily dissolved by hydrochloric acid at ordinary temperatures. For reasons stated above I was unable to devise a method of making quantitative determinations of the metallic and non-metallic form of the dispersed metal. Yet I am of the opinion that though the metal will in time be affected by the liquid, the initial quantity of metallic combinations is too small to be determined by chemical methods. It has been stated above that the disperse phase of Zn- and Cd-alcosols forms in a few weeks a white substance of hydrate or alcoholate. As stable alcosols of other metals are not subject to a similar change, it must be concluded that the particles of the sols mentioned consist in beginning of practically pure metal.

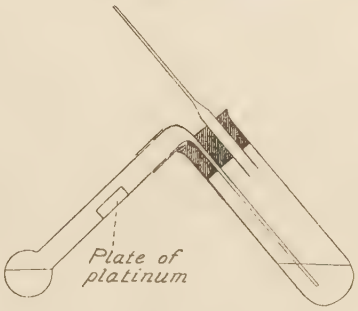

Fig. 20.

In conclusion we will touch upon the question whether the experimental conditions influence the degree of purity. Some indication as to the purity of the disperse phase is offered by the absorption of light as well as by the appearance of the sol, since, as we have seen above, the sols of Cd discolour in time. A sol produced at —75° is nearly black, whereas a sol produced at the temperature of the room is dark-brown. Accordingly it is probable that the latter is more affected by the liquid than the former. Further it may be observed that a C-sol of Cd is as

grey as an old O-sol of the same metal. Hence I conclude that in C-sols the film of hydrate or alcoholate on the particles is thicker than in O-sols. A W-sol produced at the temperature of the room is as black as an O-sol produced at —75°. Besides, the wave current develops less gas per mg. dispersed metal than does the O-current. These circumstances indicate that W-sols are purer than O-sols.

Taking into consideration the development of gas as a measure of the decomposition of the disperse medium we can now sum up our observations regarding the purity of electric alcosols as follows.

1) The bulk of the disperse phase is in all cases pure metal.
2) O-sols and W-sols are purer than C-sols.
3) The purest O-sols are obtained under the following conditions:

Pure and dry alcohol;
low temperature
great capacity
small length of arc
small self-induction.

37. *Observations under the Ultramicroscope.* — I employed a Zsigmondy slit ultramicroscope. Source of light, arclamp. Computation volume 384 μ^3.

The results were anything but regular, the cause of which could not be discovered, as I was of the opinion that the size of the particles of a sol remained constant. Most electric sols show, in addition to several particles of various intensity of light, a Tyndall cone which cannot be resolved into particles by diluting the sol. An O-sol of Cd of the concentration 1,46 mg. per ccm. was successively diluted 100, 200, 400, 800 times. At the last dilution there were scarcely any particles to be seen, the feeble Tyndall cone being the only sign of the existence of particles in the liquid. An attempt was made to produce a sol of Au that was to contain no discernible particles at all. After experimenting in various directions I arrived at the result that the number of visible particles decreased with the decrease of capacity and intensity. Under the following conditions the sol produced after 24 hours contained practically only amicrones.

Temp. —70°
C = $0{,}4 \cdot 10^{-3}$ M. F.
I_{eff} 0,35 amp.
length of arc, 0,02 ccm.
concentration, 0,145 mg. per ccm.

A sol of Cd was produced under similar conditions. The concentration was 0.2 mg. per ccm. The sol was examined after 20 hours. It was then not absolutely free from submicrones, but their number was very small.

In Sn- and Bi- alcosols no Tyndall cone could be perceived. Consequently the average radius of the particles could be determined by counting them in the ultramicroscope. The sols examined were produced at the temperature of the room, and with the capacity $3{,}2 \cdot 10^{-3}$ M. F., intensity about 1,4 amp., and length of arc about 0,3 mm. Se Table XXX.

Table XXX.

Metal	Conc. mg per ccm.	Age	r
Sn	1,08	2 days	38 $\mu\mu$
»	1,0	10 »	55 »
Bi	0,2	2 »	47 »
»	»	20 »	80 »

The examination with the ultramicroscope was not continued. A systematic investigation of the subject will be found in Chapter VII.

The results of the ultramicroscopic observations may be summarized as follows.

1) Stable alcosols in general contain submicrones as well as amicrones.
2) Alcosols of Sn and Bi present only submicrones.
3) The size of the particles is not constant.
4) Under the following experimental conditions the O-sols of Au and Cd contained very few submicrones:

Low temperature
low concentration
small capacity
feeble intensity of current.

CHAPTER VI.

Gilding of Ultramicroscopic Particles of Colloids.

38. The process used by R. Zsigmondy of producing gold-hydrosols by means of nuclei of gold has also been applied to other metals. Lüppo-Cramer[1] has reduced silver on nuclei of silver, Skita and Meyer[2] palladium on nuclei of palladium. In addition Zsigmondy and Lottermoser[3] have shown that silver is reducible on gold nuclei. As far as I am aware, no attempts to use as nuclear liquids colloids other than those mentioned above have been published.

My investigation of the size of particles of electric sols suggested to me the possibility of using the alcosols of the various metals as nuclear liquids, in order to find out their degree of dispersity. In this chapter I shall give an account of my observations, which have already been published in Koll. Z. 27, 18 (1920).

In accordance with Doerinckel's[4] process I used hydrogen peroxide as a reducing agent, which according to Westgren's[5] investigation is reliable.

39. *Metal Alcosols as Nuclear Liquids.* — Some preliminary experiments with Au- and Pt- alcosols showed a very smooth and rapid course of reduction. The gold solution always contained some alcohol, which was the disperse medium of the nuclei. I had therefore to find out the influence of the alcohol on the reduction process. Three experiments were made. In all cases 1 ccm. alcohol was added to 50 ccm. of a 10^{-3} N solution of $HAuCl_4$.

[1] Lüppo-Cramer, Koll.-Zeitschr. **7**, 99 (1910).

[2] Skita and Meyer, Ber d. Deutsch. Chem. Ges. **45**, 3,579 (1912).

[3] R. Zsigmondy and A. Lottermoser, Zeitschr. f. physik. Chem. 56, 77 (1906).

[4] F. Doerinckel, Zeitschr. f. anorg. Chem. 63, 344 (1909).

[5] A. Westgren, Zeitschr. f. anorg. Chem. 93, 151 (1915).

1) At the temperature of the room three drops of 30-per cent H_2O_2 were added. After 20 min. there was still no colour to be seen. After about 1 hour, however, a hydrosol of high dispersity had formed.

2) After three drops of H_2O_2 had been added, the solution was left alone for 15 min., and was then slowly heated with a Bunsen flame. At 40° the reduction was manifest, and a hydrosol of a radius of about 50 $\mu\mu$ was rapidly formed.

3) At 40° 3 drops of H_2O_2 were added, and the temperature was kept constant by slight heating. After 4—5 min. a hydrosol was rapidly formed, which turned out to be identical with that of the second experiment.

Thus if the reaction is rapid the alcohol has no influence, at any rate when experimenting at the temperature of the room. When nothing else is stated the temperature of the water was not higher than 25° during my experiment. As will be seen from the following, the rate of reduction was much more rapid when nuclei were added than when only alcohol was present.

The alcosols were produced by means of oscillatory discharges, according to Svedberg's method[1]. In most cases the vessel containing the disperse medium was cooled during the pulverisation with ether and solid carbon dioxide, as some metal alcosols are not durable if produced at the temperature of the room. Before being used as nuclear liquids the alcosols were diluted to the concentration required. Out of the solution thus produced 1 ccm. was added to the reduction mixture in each case. Thus there was always 1 ccm. alcohol present. The size of particles was generally calculated according to Stokes's equation by measuring the falling velocity of the top layer.

Symbols.

K = quantity of nuclear liquid of the original solution.
AuA = solution of $HAuCl_4$, 10^{-2} normal.
k = weight of nuclei in the hydrosol produced for measuring the size of particles.
p = total weight of the particles in the hydrosol.

[1] The Svedberg, Studien zur Lehre von den kolloiden Lösungen (Nova Acta reg. soc. sc. Upsaliensis [4] **2**, N:r 1, 1907).

S = specific gravity of particles.
η = viscosity of water.
t = time of falling velocity in hours.
h = height of fall.
r = radius of particles in sedimenting hydrosol in $\mu\mu$.
r_k = radius of nuclei.

Gold

Conditions of production.

$T = -70°$
$C = 0{,}4 \cdot 10^{-3}$ MF.
I = 0,35 amp.
A = 0,02 mm.

concentration after 26 hours 0,145 mg. per ccm. After 2 weeks the concentration was unchanged. The experiments were carried out in the following way. The gold solution AuA having first been diluted with water, H_2O_2 and nuclear liquid were rapidly added.

The composition of the reduction mixtures will be clear from the following scheme.

	Volumes		Weights	
1)	1 ccm.	Nuclei	0,145	mg.
	5 »	Au A	9,85	»
	44 »	Water		
	50 ccm.		10,00	mg.
2)	0,125 ccm.	Nuclei	0,0181	mg.
	0,875 »	Alcohol	9,85	»
	5 »	AuA		
	44 »	Water		
	50 ccm.		9,87	mg.

These hydrosols were used once more as nuclear liquids.

3)	2 ccm.	Sol 1)	0,40	mg. (= 0,0058 mg. orig. nuclei)
	5,2 »	Au A	10,24	»
	51,8 »	Water		
	59 ccm.		10,64	mg.

	Volumes		Weights
4)	10 ccm.	Sol 2)	1,97 mg. (= 0,00362 mg. orig. nuclei)
	7 »	Au A	13,79 »
	63 »	Water	
	80 ccm.		15,76 mg.

The hydrosols were produced 26 hours after the production of the Au-alscosols, and then the size of particles of sols 3 and 4 was determined. The following experiments were carried out 2 weeks later.

	Volumes		Weights
5)	0,1 ccm.	Nuclei	0,0145 mg.
	0,9 »	Alcohol	
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,86 mg.

	Volumes		Weights
6)	0,05 ccm.	Nuclei	0,00725 mg.
	0,95 »	Alcohol	
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,86 »

Now it is possible from the size of particles of sols 3 to 6 to determine the size of particles of the nuclei, provided spontaneous formation of nuclei is excluded. In fact the radius of the nuclei can be calculated from the formula:

$$r_k = r \sqrt[3]{\frac{k}{p}}$$

The result will be found in Table XXXI. It must be noted that k signifies here the quantity of nuclei added to the Au-hydrosol first produced.

Table XXXI.[1])

No	K	Sedimenting Sol							r_k	Diff.
		k mg	p mg	t hrs	h cm	T	η	r		
3 (1)	1 cc.	0,0058	10,64	40	1,8	12,5°	0,0122	62	5,0	— 0,2
4 (2)	0,125 »	0,0036	15,76	»	2,3	»	»	70	4,3	+ 0,5
5	0,1 »	0,0145	9,86	48	1,0	9°	0,0133	44	5,1	— 0,2
6	0,05 »	0,0073	9,86	»	1,6	»	»	55	5,0	— 0,1

Mean value $r_k = 4{,}9$ $\mu\mu$.

Cadmium and Zinc.

Conditions of production.

$T = 70°$
$I = 1{,}7$ amp.
$C = 3{,}2 \cdot 10^{-3}$ MF.
$A = 0{,}25$ mm.

Under the slit ultramicroscope the sols, besides some submicrones, also presented a Tyndall cone which could not be resolved, even if diluted 500 times.

Cadmium.

After 30 hours the concentration of the Cd-alcosol was 0,94 mg. per ccm. The reduction mixtures contained:

	Volumes	Weights
1)	1 ccm. of Nuclear liquid	0,94 mg.
	5 » Au A	9,85 »
	44 » Water	
	50 ccm.	10,79 mg.
2)	0,2 ccm. Nuclear liquid	0,19 mg.
	0,8 » Alcohol	
	5 » Au A	9,85 »
	44 » Water	
	50 ccm.	10,04 mg.

[1]) The viscosity of water of sols 5 and 6 had increased 5 per cent on account of the presence of alcohol. The values r_k have been corrected in conformity with this change. Where it has been found necessary this correction has been noted in the series below.

	Volumes		Weights
3)	0,125 ccm.	Nuclear liquid	0,12 mg.
	0,875 »	Alcohol	
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,97 mg.
4)	0,1 ccm.	Nuclear liquid	0,094 mg.
	0,9 »	Alcohol	
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,94 mg.
5)	0,02 ccm.	Nuclear liquid	0,019 mg.
	0,98 »	Alcohol	
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,87 mg.
6)	$^{1}/_{64}$ ccm.	Nuclear liquid	0,0147 mg.
	$^{63}/_{64}$ »	Alcohol	
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,86 mg.

An experiment with 1 ccm. alcosol, diluted 200 times, giving a hydrosol of higher dispersity than No 6, was rejected. The hydrosols obtained in 4 to 6 could be determined directly by means of measuring the sedimentation velocity. The sols 1 to 3 were used once more as nuclear liquids according to the following scheme.

	Volumes		Weights	
7)	1 ccm.	Sol 1)	0,216 mg.	(= 0,019 mg. orig. nuclei)
	6,3 »	Au A	12,40 »	
	56,7 »	Water		
	64 ccm.		12,62 mg.	
8)	5 ccm.	Sol 2)	1,00 mg.	(= 0,019 mg. orig. nuclei)
	5 »	Au A	9,85 »	
	45 »	Water		
	55 ccm.		10,85 mg.	

	Volumes		Weights
9)	6 ccm.	Sol 3)	1,20 mg. (= 0,014 mg. orig. nuclei)
	4,2 »	Au A	8,27 »
	37,8 »	Water	
	48,0 ccm.		9,47 mg.

If we assume a spherical shape, it is possible to calculate the radius of the nuclei from the size of the particles, provided attention is paid to their specific gravity. The volumes being inversely proportional to the specific gravity, we get

$$r_k = r_{observed} \sqrt{\frac{k}{p} \cdot \frac{S}{s}},$$

where S and s signify the specific gravities of the particle and of the nucleus in question. The influence of the specific gravity of the nuclei on the specific gravity of the particles produced was left out of consideration, the mass of nuclei in the Au-particles being insignificant.

Zinc.

The concentration was determined after 30 hours. The zinc was weighed as oxide. Concentration 0,4 mg. per ccm.

The reduction mixtures contained:

	Volumes		Weights
10)	1 ccm.	Nuclear liquid	0,40 mg.
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		10,25 mg.
11)	1/8 ccm.	Nuclear liquid	0,05 mg.
	7/8 »	Alcohol	
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,90 mg.
12)	1/64 ccm.	Nuclear liquid	0,0063 mg.
	63/64 »	Alcohol	
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,86 mg.

Table XXXII Cd.

Conc. of nuclear liquid 0,98 mg/ccm. $T = 12{,}5°$ $\eta = 0{,}0122$.

Nr.	K	Sedimenting Sol					r_k	Diff.
		k	p	t	h	r $\mu\mu$	$\mu\mu$	
1 (7)	1 cc.	0,019	12,62	40 hrs	2,2	68	9,8	0,0
2 (8)	0,2 »	0,019	10,85	45 »	1,8	58	9,1	0,7
3 (9)	0,125 »	0,014	9,48	40 »	2,1	66	9,9	0,1
4	0,1 »	0,094	9 94	45 »	0,8	38	10,9	0,8
5	0,02 »	0,019	9,87	45 »	1,8	58	9,6	0,4
6	0,0156 »	0,015	9,86	40 »	1,7	59,5	8,1	

Mean value of the first five determinations $r_k = 9{,}9$ $\mu\mu$. In the last one spontaneous formation of nuclei seems to have come into play.

13)	1	ccm.	Sol 10)	0,205 mg. (= 0,008 mg. orig. nuclei)
	6,3	»	Au A	12,40 »
	56,7	»	Water	
	64	ccm.		12,61 mg.

The result of the determinations is given in Tables XXXII and XXXIII.

In order to be able to compare the results obtained by the sedimenting method with those obtained by the method of counting particles under the slit ultramicroscope, I made another series of determinations on a Cd-alcosol.

Table XXXIII Zn.

Concentration of nuclear liquid 0,40 mg/ccm. $T = 12{,}5°$; $\eta = 0{,}0122$.

Nr.	K	Sedimenting Sol					r_k	Diff.
		k	p	t	h	r $\mu\mu$	$\mu\mu$	
10 (13)	1 cc.	0,0080	12,61	15 hrs	1,2 cm.	82	9,7	— 0,1
11	1/8 »	0,050	9,90	56,5 »	1,2 »	42	10,1	+ 0,3
12	1/64 »	0,0063	9,86	15 »	1,1 »	78	9,5	— 0,3

Mean value $r_k = 9{,}8$ $\mu\mu$.

Conditions of production of the alcosol:

$T = -70°$
$C = 12{,}8 \cdot 10^{-3}$ MF.
$I = 1{,}7$ amp.
$A = 0{,}10$ mm.

The concentration was determined after 36 hours and then contained 0,68 mg. per ccm.

The Au-hydrosols were all produced on the Cd-nuclei without interlinks. The experimental results of the two methods of determination are to be found in Tables XXXIV and XXXV. The volume of the reduction mixtures was in all cases 50 ccm., the quantity of gold 9,85 mg.

Table XXXIV Cd.

$T = 11°$ $\eta = 0{,}0127$.

Nr.	K	k	p	t	h	r	r_k	Diff.
13	0,2	0,135	9,99	43	0,65	36	11,4	+ 0,4
14	0,1	0,068	9,92	43	0,85	42	10,7	— 0,3
15	0,05	0,034	9,88	43	1,5	55	11,0	0,0
16	0,025	0,017	9,87	43	2,3	68	10,9	— 0,1

Mean value $r_k = 11{,}0\ \mu\mu$.

Table XXXV Cd.

Slit ultramicroscope. Arc lamp.

Computation volume 384 μ^3.

Nr.	K	n_1	n	n/K	Diff.
13	0,2	24,3	$31{,}7 \cdot 10^{11}$	$15{,}8 \cdot 10^{12}$	— 0,3
14	0,1	12,4	$16{,}1 \cdot 10^{11}$	$16{,}1 \cdot$ »	0,0
15	0,05	6,3	$8{,}2 \cdot 10^{11}$	$16{,}4 \cdot$ »	+ 0,3

Mean value $n/K = 16{,}1 \cdot 10^{12}$.

The value $\frac{n}{K}$ is obviously the number of particles per ccm. of the cadmium alcosols. The concentration amounting to 0,68 mg. per ccm., the number of particles per g. of Cd is calculated as:

$$N = \frac{16{,}1 \cdot 10^{12}}{0{,}68 \cdot 10^{-3}} = 2{,}36 \cdot 10^{16}$$

and the radius as:

$$r_k = \sqrt[3]{\frac{3}{4 \cdot \pi \cdot 8{,}66} \frac{1}{2{,}36 \cdot 10^{16}}} = \sqrt[3]{1{,}17 \cdot 10^{-18}} = 1{,}05 \cdot 10^{-6} \text{ cm.}$$

or $r_k = 10{,}5\ \mu\mu$,

which agrees well with the results above.

So far it has been assumed that each particle of metal of the electric sol acts as a nucleus of the Au-particles produced. The results above verify this assumption, at least in as much as the number of particles of the hydrosols formed must be proportional to the quantity of metal alcosol, and that within wide limits. Otherwise one would not, as a result of the calculation, get the same values of the radii of the nuclei. I estimate the errors of observation of the height of fall at about 10 per cent at least. The errors as to the radii of the sedimenting sols will accordingly be about 5 per cent. Thus the discrepancies correspond fairly well to the degree of inaccuracy of the method.

The particles of Cd and Zn behave quite like those of Au, if added to an Au-solution and then reduced with H_2O_2. I therefore consider it permissible to characterise these particles as nuclei in Zsigmondy's sense. After arriving at the results above, it is scarcely surprising that other metals also show the same properties as cadmium and zinc.

Silver and Copper.

The alcosols of these metals were not stable, so their nuclear effect had to be examined immediately after pulverisation. The metals in question being very difficult to pulverise, the concentration cannot be made high enough to allow an analytical determination. It must therefore be calculated from the loss of weight of the electrodes. The sedimenting part of the sols could not be taken into account. As a rule the sediment seems to be small as far as silver and copper are concerned.

Silver.

Conditions of production.

$T = -65°$
$C = 3{,}2 \cdot 10^{-3}$ M. F.
I = 1,6 amp.
A = 0,2 mm.

Concentration: 0,16 mg. per ccm.

Immediately after the dispersion the alcosol was heated to about 0°.

The reduction mixtures contained:

	Volumes		Weights
1)	1 ccm.	Nuclear liquid	0,16 mg.
	5 »	Au A	9,85
	44 »	Water	
	50 ccm.		10,01 mg.
2)	1/8 ccm.	Nuclear liquid	0,02 mg.
	5 »	Au A	9,85
	44 7/8 »	Water	
	50 ccm.		9,87 mg.

The alcosol used in the second experiment was diluted with water instead of alcohol to the concentration required, before being added to the Au-solution; this can hardly, however, have influenced the reduction. Sol 1 was used once more as a nuclear liquid.

	Volumes		Weights
3)	5 ccm.	Sol 1)	1,00 mg. (= 0,016 mg. orig. nucl.)
	5 »	Au A	9,85 »
	45 »	Water	
	55 ccm.		10,85 mg.

Copper.

Conditions of production.

$T = -70°$
$C = 3{,}2 \cdot 10^{-3}$ M. F.
I = 1,6 amp.
A = 0,25 mm.

Concentration: 0,12 mg. per ccm.

The alcosol was added without heating to the Au-solution immediately after pulverisation.

Reduction mixture:

	Volumes		Weights
4)	1 ccm.	Nuclear liquid	0,12 mg.
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,97 mg.

The alcosol being first heated to about 0^0, it was then diluted with alcohol to 8 ccm.

Reduction mixture:

	Volumes		Weights
5)	0,125 ccm.		0,015 mg.
	0,875 »	Alcohol	
	5 »	Au A	9,85 »
	44 »	Water	
	50 ccm.		9,86 mg.

In the fifth experiment the Cu-alcosol, originally dark-brown, seemed to have grown lighter. I waited for 10 min. before producing sol 6. Then the Cu-sol had got a reddish brown colour, remaining, however, quite clear. Not even in reflected light could any turbidity be perceived.

6) Reduction mixture as in 4).

The hydrosols obtained in 4 and 6 were again used as nuclear liquids.

Reduction mixtures:

	Volumes		Weights	
7)	5 ccm.	Sol 4)	1,00 mg.	(= 0,012 mg. orig. nuclei)
	5 »	Au A	9,85 »	
	45 »	Water		
	55 ccm.		10,85 mg.	
8)	5 ccm.	Sol 6)	1,00 mg.	(= 0,012 mg. orig. nuclei)
	5 »	Au A	9,85 »	
	45 »	Water		
	55 ccm.		10,85 mg.	

The falling velocity of hydrosols 5, 7 and 8 could now be determined. The sols were all stable.

The results will be seen in Table XXXVI.

These results are interesting. The table shows how the increase of the particles appears in course of time. The alcosols coagulated to form a typical gel, which had a very loose and transparent structure. Hence I am convinced that we are concerned here with secondary particles of a very loose structure, which undergo a gradual increase. Now these particles, as long as they have not increased too much, seem to be available as nuclei for producing stable Au-hydrosols, thus enabling us to determine their size.

Accordingly it may be possible, by producing Au-hydrosols, to fix the stages of coagulation at any time, which would give us a method to follow the process in the amicroscopical sphere.

Tin and Bismuth.

Alcosols of these metals are so coarse that if stable (which is not always the case) they can be counted under the ultramicroscope.

A tin-alcosol containing 0,5 mg. per ccm. was used. To 50 ccm. of a 10^{-3} N Au solution were added 1, 0,2 and 0,1 ccm. respectively of the nuclear liquid. The colour of the first hydrosol was blue, in incident light dark-brown. The second experiment gave a rather coarse hydrosol of a much darker colour than that of a pure Au-hydrosol of a corresponding degree of disper-

Table XXXVI.

$T = 12{,}5°$ $\eta = 0{,}0122$.

	Nr.	K	Sedimenting Sol					r_k
			k	p	t	h	r	
Ag.	3 (1)	1,0	0,016	10,85	42,5	1,75	52	7,1
	2	1/8	0,020	9,87	15	2,5	118	18
Cu.	7 (4)	1	0,012	10,85	23	0,4	38	5,0
	5	1/8	0,015	9,86	68	1,3	40	6,0
	8 (6)	1	0,012	10,85	23	0,8	54	7,8

sity. The third experiment gave a coarse hydrosol of about the same colour as that of a pure Au-hydrosol. Only the last-mentioned was stable for a sufficient time to allow the estimation of the falling velocity.

$$t = 2 \text{ hours}$$
$$h = 1{,}0 \text{ cm.}$$
$$T = 11{,}5^\circ$$
$$\eta = 0{,}0125$$

These data correspond to a radius of about

$$r = 200\ \mu\mu.$$

The radius of the nuclei will be:

$$r_k = 200 \sqrt[3]{\frac{0{,}05}{9{,}90} \cdot \frac{19{,}3}{7{,}3}} = 47\ \mu\mu.$$

Previously, with another sol produced under somewhat different conditions, I had got the value of

$$r_k = 59\ \mu\mu$$

whereas the counting under the ultramicroscope gave the value 55 $\mu\mu$.

Bismuth behaves similarly. To 50 ccm. of an Au-solution, containing 9,85 mg. Au, was added 1 ccm. of a bismuth alcosol containing 0,35 mg. per ccm. The hydrosol obtained was very coarse.

$t = 2$ hours	$S = 18{,}7$
$h = 0{,}8$ cm.	$k = 0{,}35$ mg.
$T = 15^\circ$	$p = 10{,}2$ »
$\eta = 0{,}012$	$r = 180\ \mu\mu.$

$$r_k = 180 \sqrt[3]{\frac{0{,}35}{10{,}2} \cdot \frac{18{,}7}{9{,}8}} = 76\ \mu\mu.$$

About the same value was obtained from my ultramicroscopical determinations of bismuth alcosols. See section 37.

Though these sols are not suitable for accurate measurements, the results above might be of some importance as showing that the »nuclear effect» cannot be ascribed to the decomposition products of the alcohol.

Other metals.

Finally I have examined the nuclear effect of electric alcosols of mercury, aluminium, and iron. Antimony could not be used, as it coagulated immediately after the dispersion.

The mercury alcosol was produced in the following way. Two copper rods were purified with hydrochloric acid, and their ends dipped into mercury. On taking them out some mercury adhered to the ends. The electrodes so prepared being fitted into the arc micrometer, the apparatus was put into the cooled pulverisation vessel. After the mercury had frozen, the pulverisation could be carried out as usual. Concentration 1,1 mg. per ccm.

1) To 50 ccm. of a 10^{-3} N Au-solution was added, as usual, 1 ccm. of the sols and the reduction mixture was afterwards mixed with H_2O_2. A rather high disperse hydrosol formed, with a deep violet colour, in reflected light brownish. The radii of the particles were estimated at 20—30 $\mu\mu$. After some time there had formed at the bottom of the flask a dirty sediment, which could not be shaken up. This indicates that, besides the ultramicrones, there were also present in the alcosol large drops of mercury, which had united with the gold.

2) To 50 ccm. of a 10^{-3} N Au-solution was added as a nuclear liquid 1 ccm. of the alcosol, diluted with alcohol to 8 ccm. The hydrosol obtained had the ordinary appearance of an Au-hydrosol 60 $\mu\mu$ in radius. The sediment was now small.

The presence of the sediment rendered an exact determination difficult in this case, so I did not pursue it. The hydrosols obtained were stable.

Al- and Fe-alcosols also behaved in the usual way during the reduction. Two experiments were made on them. 1 and $^1/_8$ ccm. respectively of the alcosols were used as nuclear liquids. The appearance of the hydrosols clearly showed that the solution to which had been added small quantities of nuclei contained the largest particles. The hydrosols obtained coagulated rapidly after the production.

40. *Probable Action of the Nuclei.* —

In order to obtain comparable values of the time of reduction, one has not only to make the experiments at a constant temperature, but uniformity in the size of the particles and the concentration of the different sols is indispensable. I have not

carried out any investigation on this matter. Still my observations on the time of the reduction may help to throw light upon the phenomenon under consideration.

Even at the first experiment I was struck by the fact that the formation of sols took place so rapidly. Often the coloration of the liquid was visible in less than 1 minute, and in no case did I have to wait more than 5 minutes before the hydrosol had assumed its definite appearance. In the case of copper and aluminium the liquid, at the first experiment, turned reddish violet within 10 seconds, with silver after 25, with mercury after 30 seconds. In particular it struck me that when using tin particles as nuclei the sol become quite visible even within 1 min., though the number of tin nuclei was very small. I got the impression that, with regard to the rapidity of action, the gold nuclei are inferior to most of the metals tested.

I regard that circumstance as supporting an assumption I held from the very beginning of my researches. It is striking that of all metals gold has the lowest electrolytic solution pressure. Now metallic particles of electrolytic solution pressure send ions into the solution, and instead of these gold molecules settle on the particles of metal, i. e. the amicrones have been gilded. They then behave as ordinary Au-nuclei.

Now if the action in the initial phase were an electrolytic one, one would expect that metals of a high solution pressure would have the most rapid action. This, however, was very probably not the case in my experiments. In the case of zinc and cadmium I had to wait about 1 min. before the phenomenon appeared. If my hypothesis is correct, the behaviour of these metals will, however, be easily explained. Electric sols of Zn and Cd, if left to themselves for some days or weeks (according to the conditions of production) will grow more and more pale, and finally quite white. In fact a zinc hydrosol, produced at ordinary temperature, will become quite white within a few hours.

It has so far been left an open question as to whether the particles of metal are covered with a layer of oxide or not. If we assume, however, that this is the case, then the layer of hydrate or alcoholate must be dissolved or the ions of metal must diffuse into the liquid before the electrolytic nuclear action can be brought about. In both cases a delay of the nuclear action must be caused. The strange behaviour of Zn- and Cd-nuclei has

therefore not caused me to reject my hypothesis; it has only persuaded me that the particles of these colloids are covered with a layer of oxide. I do not even consider that it is impossible, by careful observations as to the the time of nuclear action, to discover a method of testing the purity of ultramicrones of metal.

41. *Other colloids.* —

Arsenic trisulphide.

The colloids were produced according to Picton and Linder's procedure.

A) In 100 ccm. water was dissolved 0,2 g. As_2O_3, so that the solution was 10^{-2} N. The solution having first been cooled, H_2S was transmitted through it. After the As_2S_3-hydrosol had been formed, the H_2S was expelled with hydrogen, and the hydrosol then filtered.

The hydrosol was turbid; in the slit ultramicroscope feeble submicrones were visible. Concentration 2,3 mg. per ccm.

The following experiments were carried out.

	Volumes		Weights
1)	0,5 ccm.	Nuclear liquid	1,16 mg.
	2,5 »	Au A	4,93 »
	47 »	Water	
	50 ccm.		6,09 mg.
2)	0,2 ccm.	Nuclear liquid	0,46 mg.
	2,5 »	Au A	4,93 »
	47,3 »	Water	
	50 ccm.		5,39 mg.
3)	0,1 ccm.	Nuclear liquid	0,23 mg.
	2,5 »	Au A	4,93 »
	47,4 »	Water	
	50 ccm.		5,16 mg.

The number of particles of the hydrosols obtained was determined by counting the particles under the slit ultramicroscope. The size of particles of the hydrosols 2 and 3 was also determined by means of sedimenting. Because of the great proportion of As_2S_3 the change of the specific gravity caused by the presence of that substance has to be taken into account. I assumed 3,4 to be the specific gravity of arsenic trisulphide. See Table XXXVII.

Table XXXVII.

$T = 11{,}5°$ $\eta = 0{,}0125$.

Nr.	K	k	p	S	t	h	r	r_k
2	0,2	0,46	5,39	13,8	42	1,1	57	40
3	0,1	0,23	5,16	16,0	18	0,7	64	38

Mean value $r_k = 39$ $\mu\mu$.

Table XXXVIII.

Slit ultramicroscope; Arc lamp. Computation volume 384 μ^3.

Nr.	K	n_1	n	n/K	Diff.
1	0,5	9,5	$12{,}4 \cdot 10^{11}$	$24{,}8 \cdot 10^{11}$	— 0,1
2	0,2	3,7	4,8 »	24,0 »	— 0,9
3	0,1	2,0	2,6 »	26,0 »	+ 1,1

Mean value $n/K = 24{,}9 \cdot 10^{11}$.

In Table XXXVIII n_l indicates the number of particles (mean value of 100 enumerations) in the computation volume. This refers to the original Au-hydrosol; n indicates the number of particles in the total Au-hydrosol.

From the concentration of the As_2S_3-hydrosol as well as from the value of $\frac{n}{K}$, which will obviously represent the number of particles of the nuclear liquid per ccm., it is possible to calculate the mass of the nuclei, and also their radius, spherical shape being assumed. As above, the specific gravity is estimated to be 3,4. The number of particles per g. of the substance will be:

$$N = \frac{24{,}9 \cdot 10^{11}}{2{,}3 \cdot 10^{-3}} = 10{,}8 \cdot 10^{14};$$

and the mass of particles:

$$\frac{1}{10{,}8} \cdot 10^{-14}\,\text{g; and}$$

$$r_k = \sqrt[3]{\frac{3}{4 . \pi . 3{,}4 . 10{,}8}} \cdot 10^{-14} = \sqrt[3]{64 \cdot 10^{-18}} = 4{,}0 \cdot 10^{-6}\ \text{cm.} = 40\ \mu\mu.$$

B) The hydrosol was produced from a $5 . 10^{-4}$ N solution of As_2O_3.

The hydrosol was quite clear; the bluish Tyndall cone could not be resolved under the ultramicroscope. Qualitative experiments exhibited the same behaviour of the hydrosol as that of the hydrosol previously tested. Concentration of the sol 0,125 mg. per ccm. Only one determination was carried out.

The reduction mixture contained in 50 ccm.

	Volumes		Weights
4)	0,1 ccm.	Nuclear liquid	0,0125 mg.
	2,5 »	Au A	4,93 »
	50 ccm.		4,94 mg.

Result of the determination: Table XXXIX.

C) Another series of experiments was made, with a hydrosol which had been produced from a 10^{-4} N solution of As_2O_3. Concentration of the sol 0,024 mg. per ccm.

Reduction mixtures:

	Volumes		Weights
5)	5 ccm.	Nuclear liquid	0,12 mg.
	2,5 »	Au A	4,93 »
	42,5 »	Water	
	50 ccm.		5,05 mg.
6)	1 ccm.	Nuclear liquid	0,024 mg.
	2,5 »	Au A	4,93 »
	46,5 »	Water	
	50 ccm.		4,95 mg.
7)	0,2 ccm.	Nuclear liquid	0,0048 mg.
	2,5 »	Au A	4,93 »
	47,3 »	Water	
	50 ccm.		4,93 mg.
8)	0,1 ccm.	Nuclear liquid	0,0024 mg.
	2,5 »	Au A	4,93 »
	47,4 »	Water	
	50 ccm.		4,93 mg.

Table XXXIX.

$T = 11{,}6°$ $\eta = 0{,}0125$.

Nr.	N	k	p	S	t	h	r	r_k	Diff.
4	$5 . 10^{-4}$	0,012	4,94	19,1	18	0,9	66	15,9	—
9 (5)	$1 . 10^{-4}$	0,012	5,44	19,1	41	0,9	43	10,0	— 0,6
6	»	0,024	4,95	18,9	48	0,8	37	11,3	+ 0,7
7	»	0,0048	4,93	19,3	48	2,0	59	10,4	— 0,2
8	»	0,0024	4,93	»	17,5	0,8	61	8,5	—

Mean value of 5 — 7 $r_k = 10{,}6$ $\mu\mu$.

9)	5 ccm.	Sol 5)	0,505 mg. (= 0,012 mg. orig. nuclei)
	2,5 »	Au A	4,93 »
	47,5 »	Water	
	55 ccm.		5,44 mg.

In table XXXIX N indicates the concentration (in mol.) of the original solution during the production of the As_2S_3-hydrosol in question.

In the 8th experiment the quantity of nuclear liquid added was probably too small: the spontaneous formation of nuclei had begun before the reduction was concluded.

From the results of the experiments it will be seen that the size of the particles diminishes regularly with the concentration of the solution of As_2O_3, which has, in fact, been already observed by Picton and Linder[1], and then verified by Svedberg[2] by means of measurements of the absorption of light. In this connection I wish to call attention to a relation existing between the size of particles and the concentration of the original solution of the arsenic trioxide. Provided the number of particles per ccm. of the hydrosol produced is always the same, it will be possible to test this assumption by combining the results of the above experiments. In fact, if this is the case, since the number of particles is proportional to the concentration, and inversely proportional to the third power of the radius, the radius itself must be proportional to the cubic root of the concentration, or

$$\frac{\text{concentration}^{1/3}}{\text{radius}} = \text{C (constant)}.$$

[1] H. Picton, Journ. chem. Soc. **61**. 114 (1892).
H. Picton and S. E. Linder, Journ. chem. Soc. **67**, 63 (1895).

[2] The Svedberg, Die Existens der Moleküle (Leipzig 1912), 27.

In Table XL a test of this sort has been made.

Table XL.

N	r_k Obs.	r_k Calc.	Diff. Abs.	Diff. Per cent	C	C^3
$1 . 10^{-2}$	40	44	— 4	— 10	$5{,}4 . 10^{-3}$	$156 . 10^{-9}$
$5 . 10^{-4}$	15,9	16,1	— 0,2	— 1,5	5,0 . »	125 . »
$1 . 10^{-4}$	10,6	9,4	+ 1,2	+ 12	4,4 . »	84 . »
	Mean value		$C = 4{,}9 . 10^{-3}$			

From the mean value of C r_k has been calculated according to the equation above. The differences are greater than the errors of observation. Still I do not think that I am mistaken in stating that the assumption made above is in some respects in agreement with the actual facts. For while the concentration has undergone a change of 100 : 1, the number of particles (which is proportional to C^3) has scarcely decreased in the ratio 2 : 1.

Antimony Trisulphide.

Four experiments were made on a clear hydrosol of antimony trisulphide (concentration 1,8 mg. per ccm.). To 5 ccm. AuA, diluted with water to 49 ccm., was added:

1 a) 1 ccm. of the original sol.
b) 1 » » » » »
2) 1 » » » sol diluted 5 times
3) 1 » » » » » 25 »

After reduction with H_2O_2, hydrosols 1 (a and b) were used as nuclear liquids, according to the following scheme.

4)	2 ccm. sol 1)	= 0,394 mg. Au
	5 » 10^{-2} N $HAuCl_4$-solution	= 9,85 » »
	45 » water	
	52 ccm.	10,24 mg. Au

Hydrosol 1 a was used as a nuclear liquid after 2 days, 1b after 1 hour.

Hydrosols 2 to 4 were put in the sedimenting room, and the falling velocity determined as before.

The specific gravity of Sb_2S_3 was assumed to be 4,1.

Table XLI.

Nr.	K	k	p	S	t	h	r	r_k	Diff.
4 (1 a)	1	0,07	10,31	18,8	47	2,0	63,5	20,0	+ 1,0
4 (1 b)	1	0,07	10,31	»	19	0,75	61	19,2	+ 0,2
2	0,2	0,36	10,21	17,1	46	0,55	35	18,5	— 0,5
3	0,04	0,07	9,92	18,8	23	0,8	57	18,2	— 0,8

Mean value $r_k = 19{,}0\ \mu\mu$.

From the determinations 4, 1 a, and 1 b respectively it will be seen that the hydrosols produced were fairly stable.

*

The reduction process was somewhat slower in the experiments on antimony trisulphide and arsenic trisulphide than was the case when metallic nuclei were used. The formation of sols became visible within 2 to 4 minutes. The action in this case can hardly be an electrolytic one. Though a definite explanation can be arrived at only after a close investigation, I wish to make some observations as to the striking nuclear action of the sols tested.

One may conceive that the Au-solution has been adsorbed by the particles of the colloid. Then an increase of concentration would take place in the vicinity of the particles. Accordingly the reduction would proceed more rapidly on the particles than in other parts of the liquid, i e. the particles would act as a kind of »adsorption nuclei». As a matter of fact, students of colloids are not quite unaware of an explanation to this effect. K. Hiege[1] has resorted to such an assumption when trying to explain the influence of silicic acid on the dispersity of the Au-hydrosols produced. And R. Zsigmondy[2] has adopted his opinion. Accordingly this kind of nuclear action may be a very common one. As yet I have examined only few colloids from this point of view. These experiments will now be described.

Several experiments with Fe_2O_3 and SiO_2 (the hydrosols contained about 0,1 per cent.) gave much coarser sols than could be

[1] K. Hiege, Zeitschr. f. anorg. Chem. **91**, 145 (1915).

[2] R. Zsigmondy, Kolloidchemie, 2 Auflage (Leipzig 1918), 212.

expected. The reaction went on very slowly. Parallel experiments with the colloids in question as »nuclear liquids» as well as without them showed that the reduction after adding Fe_2O_3 or SiO_2 proceeded hardly more rapidly than in a solution without nuclei. The degree of dispersity presented no difference from that of solutions without nuclei

On the supposition that I had to deal with a sort of absorption, I made the following experiment. 1 ccm. of the SiO_2-sol was diluted with water. To this liquid was added 2 ccm. of a very high disperse Au-hydrosol (Au P), and the liquid was then diluted to 100 ccm. After 20 hours 5 ccm. of a 10^{-3} N solution of $HAuCl_4$ was added to the liquid. Simultaneously I produced an Au-solution of the same volume and the same concentration, to which was also added 2 ccm. Au P. After some few drops of H_2O_2 had been added, the reduction of both solutions proceeded equally rapidly and the hydrosols produced presented the same appearance. An experiment on a sol of Sb_2S_3, which was carried out in much the same way, gave the same result. These experiments indicate that at least Au-particles are not to any great extent adsorbed by the substances in question. Otherwise the degree of dispersity would be different in the various cases.

Finally I have examined gelatine, gum arabic, Congo red, and a tin acid hydrosol (peptised with NH_3) as to their nuclear action. All of them gave a negative result. My researches as to the eventual nuclear action of sulphur hydrosols are not concluded. They have all, however, yielded a positive result, which is rather striking in connection with K. Hiege's[1] results.

It may also be mentioned that K. Hiege has arrived at an opinion different from mine with regard to the influence of SiO_2 on the degree of dispersity.

[1]) K. Hiege, loc. cit.

CHAPTER VII.

Size of Particles of Electric Sols.

42. *Further Experiments on the Gilding Method.* — The results of the gilding method, as applied to Sn- and Bi- sols, (see section 39), have indicated that the decomposition products of the medium have no influence on the size of the particles of the Au-hydrosol produced. In order to prove the tenability of this conclusion in another way, I made the following experiment. An O-sol of Sb was produced at the temperature of —75° and with the capacity $3{,}2 \cdot 10^{-3}$ MF; I_{eff}, 1,1 amp; length of arc 0,3 mm. The pulverisation continued for 2 minutes. In a few minutes the sol had coagulated.

The clear filtrate was tested as to its nuclear effect. To the usual reduction mixture was added 0,1 ccm. of the filtrate; the beginning of the reduction was visible after 11 minutes. Simultaneously a parallel experiment was made, in which instead of the filtrate the same quantity of pure alcohol was taken. In this experiment the reduction was visible after 8 minutes. When 0,5 ccm. was added to the reduction mixture the reduction was visible after 7 minutes. As the dispersion had been going on about 4 times as long as in the following experiments, it must be concluded that the liquid contained a sufficient quantity of the decomposition products to make the negative result of the test reliable.

In the preceding chapter an explanation of the nuclear effect of metallic particles was proposed, according to which the effect was thought to be an electrolytic one. If this explanation were tenable we should expect a reduction effect, though certainly a very slight one, even if H_2O_2 is not added to the solution. In fact if 1 ccm. of a Cd-alcosol of the concentration 0,52 mg. per ccm. is added to 50 ccm. of a 0,5 N $H\,Au\,Cl_4$-solution, an unmistakable touch of pink colour can be observed after 15 minutes. However, in making a similar experiment with an Au-alcosol instead of the Cd-alcosol, the result was about the same. I

also tested alcohol, in which an arc between electrodes of carbon had been burning for 4 minutes. Here too a slight reduction effect was perceived, though only after 10 hours. Thus we must conclude that the liquid has obtained a certain power of reduction from the decomposition products of the medium. Accordingly I have not been able to prove the tenability of this hypothesis as to the electrolytic power of reduction of electric sols, as it was not possible to separate the electrolytic effect from the reducing effect of the decomposition products. On the other hand, with regard to the reliability of the method, the slight power of reduction of the liquid itself cannot be of much importance, as its effect seems to be slow.

43. *Increase of O-sol Particles with Time.* — The determinations in this chapter are all made in the same way by using the gilding method described in Chapter VI. The solution of $H\,Au\,Cl_4$ contained 0,01 mol. per 1,000 ccm. From this solution at each determination 2,5 ccm. was put into an Erlenmeyer flask, which was filled with pure water to such a volume that after adding the nuclear liquid, k_1, the total volume was 50 ccm. If after adding H_2O_2, the hydrosol obtained was of too high a degree of dispersity för sedimentation, the hydrosol was again used as a nuclear liquid in order to obtain a sol of suitable dispersity.

Symbols.

t = time after the dispersion at which the Au-hydrosol in question was produced,
v = velocity of the Au-particles of the sedimenting hydrosol.
T = temperature of the room where the sols were sedimenting.
D = total weight of dispersed metal, including melting globules.
c = concentration of the original alcosol, the sedimented portion not counted.
Other symbols are explained in Chapter VI.

It appears from Tables XLII and XLIII, as well as from Figs. 21—23, that to begin with, the particles grow rapidly, in some hours, however, reaching a range of relative stability. The three series of Cd. Table XLII, Fig. 21 also show that the rate of increase varies with the concentration of the sol. The higher the concentration, the larger the particles, other conditions being

Table XLII.

Electrodes Cd. Temperature — 75°. $C = 1{,}6 \cdot 10^{-3}$ M. F.
A = 0,25 mm. Volume of alcohol 60 ccm.

Symbol	t	K_1 ccm.	K_2 ccm.	T	v cm. per sec.	r $\mu\mu$	r_k $\mu\mu$
I = 1,3 amp. D = 0,0449 g. Conc. = 0,53 mg. per ccm.							
a	40^m	0,05	—	15,8°	$3{,}9 \cdot 10^{-6}$	33	7,5
b, c	80^m	0,5	2	»	12.	59	9,8
d, f	5^h	0,1	10	»	16.	68	10,8
e, g	»	0,5	2	»	15.	66	11,0
h	20^h	0,5	2	»	18.	72	12,0
I = 0,8 amp. D = 0,0220 g. Conc. = 0,23 mg. per ccm.							
a, c	30^m	0,5	1	15,8°	$13{,}2 \cdot 10^{-6}$	61	6,1
b, d	32^m	0,1	5	»	14,6	64	6,3
e, g	1^h	0,5	1	»	16,3	68	6,8
f, h	»	0,1	5	»	19,6	74	7,2
i, k	$4\,^1/_2{}^h$	0,5	1	16,0°	29	90	9,0
g	»	0,1	—	»	5,7	40	8,7
l	24^h	0,1	—	15,8°	7,2	45	9,8
I = 0,8 amp. D = 0,0063 g. Conc. = 0,075 mg. per ccm.							
a, g	5^m	0,5	1	15,7	$18{,}5 \cdot 10^{-6}$	72	5,0
b, h	10^m	0,5	1	»	17,2	70	4,9
c, i	15^m	0,5	1	»	20,5	76	5,3
d	22^m	0,1	—	»	4,9	38	5,7
e, j	30^m	0,5	1	»	24	82	5,7
f	36^m	0,1	—	»	6,2	42	6,3
k, m	2^h	0,5	—	»	Failed		
l	»	0,1	—	»	»		
n, p	5^h	0,5	2	»	26	85	7,4
o	7^h	0,2	—	»	6,0	41	7,8
q	25^h	0,5	—	»	3,8	33	8,3
r	»	0,2	—	»	6,7	44	8,3

Fig. 21.

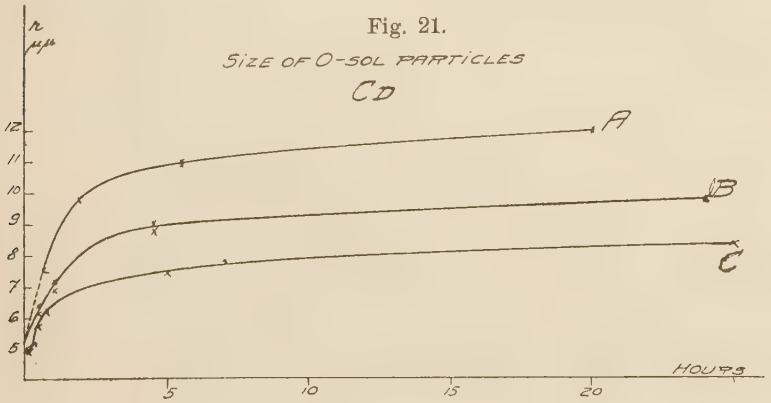

Table XLIII.

Au and Bi.

Symbol	t	K_1 ccm.	K_2 ccm.	T	v cm. per sec.	r $\mu\mu$	r_k $\mu\mu$
Au. Temp. + 17°. $C = 1{,}6 \cdot 10^{-3}$ M. F. $I = 1{,}6$ amp. $A = 0{,}25$ mm. $D = 0{,}0016$ g. Volume of alcohol 50 ccm. Conc. = 0,024 mg. per ccm.							
a_1 a_2	1^m	0,5	5	15,2	$11{,}0 \cdot 10^{-6}$	56	3,4
b	5^m	1,0	—	»	2,1 . »	25	4,3
c	15^m	0,5	—	»	11,8 . »	58	7,8
d	18^h	0,5	—	»	32 . »	96	13,0
Bi. Temp. — 75°. $C = 3{,}2 \cdot 10^{-3}$ M. F. $I = 1{,}9$ amp. $A = 0{,}3$ mm. $D = 0{,}0157$ g. Volume of alcohol 60 ccm. Conc. = 0,11 mg. per ccm.							
a.....	2^m	1,0	—	Coagulated in a few minutes			
b	5^m	0,5	—	» » » » »			
c.....	12^m	0,1	—	15,6	$38 \cdot 10^{-6}$	103	17
d	$2^1/_2{}^h$	0,1	—	»	54 . »	125	21
e.....	13^h	0,2	—	»	93 . »	161	33
f.....	140^h	0,2	—	15,2	140 . »	200	41

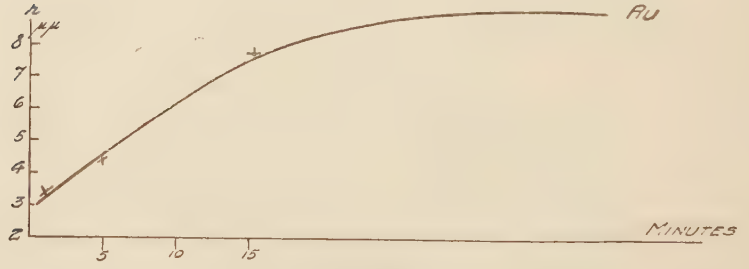

Fig. 22.

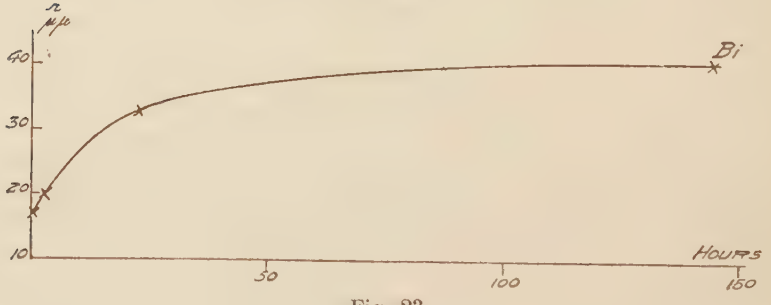

Fig. 23.

unchanged. On the other hand, on extrapolating to the time 0 after the dispersion it seems very probable that the particles are of the same size in all three cases.

Again, taking into consideration the last series in Table XLII and the curve C, Fig. 21, we see that at first, when the alcosol is cold, the size of the particles is constant, apart from errors of observation. Now, as the fate of the colloids after the dispersion is only of secondary interest to us, I shall leave that question in order to enter upon the problem of finding the initial size of the particles.

44. *Initial Degree of Dispersity of Electric Alcosols.* — When determining the size of particles immediately after producing the sols, the sedimenting portion cannot be separated from the sol proper. I have examined the influence of the melting globules on the determination by gilding the colloid before and after shaking it.

It appears from Table XLIV that the results of the parallel experiments are identical. It may be observed that the agreement is better than might be expected, considering the inaccuracy of the method. That is due to the fact that the two sedimenting vessels, one containing sol B, the other sol A, were placed beside one another in order to render a comparison possible. In this comparison hardly any difference could be observed between the falling velocities of the two corresponding sols.

Table XLIV.

Electrodes Cd. $C = 1{,}6 \cdot 10^{-3}$ M. F. $I = 1{,}45$ amp. $A = 0{,}25$ mm.
Conc. = 0,12 mg. per ccm. B = Before shaking. A = after shaking.

t Hours		K_1 ccm.	K_2 ccm.	T	T Hours	h cm.	v cm. 10^{-6} per sec.	r	r_k
5	B	0,1	—	15,7	18	0,50	7,7	47	8,2
	A	»	—	»	»	»	»	»	»
20	B	0,2	10	15,8	20,5	1,25	16,9	69	8,3
	»	0,1	—	»	»	0,55	7,5	46	8,0
	A	0,2	10	»	»	1,30	17,6	70	8,5
	»	0,1	—	»	»	0,55	7,5	46	8,0

The result mentioned can be explained theoretically as follows. Let us assume a sol containing two groups of particles

a mg. of radius r_1
b » » » r_2

and suppose further that the Au-molecules of the reduction mixture fix on the nuclei at a rate that is proportional to the surface of the nuclei. Since the volume of a particle (spherical shape assumed) is proportional to r^3, we can put

$$n_1 = \frac{a}{c \cdot r_1^3}$$

$$n_2 = \frac{b}{c \cdot r_2^3} (C = \text{const.})$$

where n_1, n_2 signify the numbers of the particles of the radii r_1, r_2.

The total surface of each group of particles will be

$$s_1 = n_1 \cdot 4 \pi r_1^2 = \frac{a}{c r_1^3} \cdot 4 \pi r_1^2 = \frac{a}{r_1} \cdot C (C = \text{const.})$$

$$s_2 = \frac{b}{r_2} \cdot C$$

So the ratio of the quantities of the gold of the reduction mixture which will fix on the two groups will be

$$\frac{s_1}{s_2} = \frac{a}{b} \cdot \frac{r_2}{r_1}$$

Let r_1 refer to the particles of the sol proper and r_2 to the melting globules. Then, as $\frac{r_2}{r_1}$ is about 100 or more, and $\frac{a}{b}$ is at any rate not much less than 1, the sediment will take only 1 per cent of the gold of the reduction mixture, a quantity that has no influence on the determination of the radius of the nuclei.

The results are to be found in Tables XLV—L; they will be discussed later.

On account of the instability of C-sols of Au the author could not make any determinations of them. C-sols of Cd, pro-

Table XLV. O-sols.

Cd. Temp. — 75°.

C M. F.	I amp.	A mm.	c mg per ccm.	t	K_1 ccm.	K_2 ccm.	T	v cm. 10^{-6} per sec.	r $\mu\mu$	r_k $\mu\mu$	Mean value of r_k
$0{,}4 \cdot 10^{-3}$	0,85	0,25	0,04	1 m	0,5	5	15,2	11,9	58	5,4	5,3
				2 »	0,1	—	»	6,0	41	5,2	
	1,2	0,25	0,06	1 1/2 m	0,5	5	15,2	9,9	53	5,7	5,6
				3 »	0,1	—	»	5,4	39	5,4	
$1{,}6 \cdot 10^{-3}$	0,9	0,07	0,128	4 m	0,5	2	15,7	0,9	53	5,5	5,4
				5 »	0,1	10	»	11,6	57	5,2	
	0,8	0,25	0,075	5 m	0,5	1	15,7	18,5	72	5,0	5,1
				10 »	»	1	»	17,2	70	4,9	
				15 »	»	1	»	20,5	76	5,3	
	1,45	0,25	0,12	2 m	0,5	1	15,7	15,6	66,5	5,4	5,4
				4 »	»	1	»	14,8	65	5,2	
				9 »	»	1	»	17,3	70	5,7	
$3{,}2 \cdot 10^{-3}$	0,85	0,25	0,045	2 m	0,5	2	15,4	15,1	66	4,8	4,9
				3 »	0,1	10	»	17,9	72	5,1	
				4 »	0,2	5	»	15,1	66	4,7	
	1,3	0,25	0,087	2 m	0,5	1	15,4	17,1	70	5,1	4,9
				3 »	0,1	5	»	16,2	68	4,8	
				4 »	0,1	5	»	16,2	68	4,8	
	1,3	0,07	0,095	2 m	0,5	5	15,2	9,0	51	6,4	6,3
				3 »	0,1	—	»	5,2	38	6,2	
	1,9	0,25	0,12	1 m	0,1	2	15,5	23	80	4,8	5,0
				2 »	0,2	1	»	27	88	5,2	
$12{,}8 \cdot 10^{-3}$	1,6	0,12	0,066	1 m	0,5	2	15,0	14,3	64	5,3	5,4
				2 »	0,1	10	»	15,9	67,5	5,4	
$90 \cdot 10^{-3}$	0,5	0,05	0,025	2 m	0,5	—	15,2	4,0	34	6,0	6,2
				6 »	0,5	—	»	4,6	36	6,4	

Table XLVI.

Cd. Temp. — 75°.

$C = 3{,}2 \cdot 10^{-3}$ M. F. $L = 2000 \cdot 10^{-8}$ Henry; $A = 0{,}25$ mm. $I = 1{,}3$ amp.
Conc. 0,14 mg/cm³.

t min.	K_1 ccm.	K_2 ccm.	T	v cm. 10^{-6} per sec.	r $\mu\mu$	r_k $\mu\mu$	Mean value of r_k
1	0,5	1	15,4	12	58	4,9	
$1\frac{1}{2}$	"	1	"	13	61	5,1	5,0
$2\frac{1}{2}$	"	1	"	13	61	5,1	

duced at the temperature of the room, did not act as nuclear liquids, probably because the particles were too much oxidised.

45. *Degree of Dispersity of S-alcosols*[1]. — The cooling tube was filled with water (+ 17°) or methyl-alcohol and solid carbon dioxide. The examination was carried out only on Ag- and Au-alcosols. The concentration of the Ag-sols was determined by evaporating to dryness a known volume of the sol, heating to redness, weighing, dissolving the silver with nitric acid, washing, and weighing once more. The concentration of the Au-sols was

Table XLVII.

Cd. Temp. + 17°.

$C = 3{,}2 \cdot 10^{-3}$ M. F. $L = 0$. $A = 0{,}25$ mm. $I = 1{,}0$ amp.

c mg per ccm.	t min.	K_1 ccm.	K_2 ccm.	t	v cm. 10^{-6} per sec.	r $\mu\mu$	r_k $\mu\mu$
0,056	1	0,5	5	14,6	10,4	55	5,8
	$2\frac{1}{2}$	0,5	5	"	13,9	63	6,6
	6	0,1	-	"	10,4	55	7,5
0,083	1	0,5	5	14,6	10,2	54	6,4
	$1\frac{3}{4}$	0,5	5	"	11,1	57	6,8
	3	0,5	"	"	"	"	6,8
	45	0,1	—	"	9,3	52	8,0

[1] See notes p. 60.

determined in a platinum crucible. After heating to redness and weighing, the silicic acid was removed with hydrofluoric acid, and the gold weighed alone. On account of the small quantities weighed (some few milligrams), the results were not very accurate. The Ag-sol contained about 60 per cent silver, the Au-sol 40 per cent gold of the total weight of the dry substance.

46. *O-sols of Different Dispersion Media.* — The author has also tried to determine the size of particles when Cd and Au were dispersed in acetone, ether, and isobuthyl alcohol. The

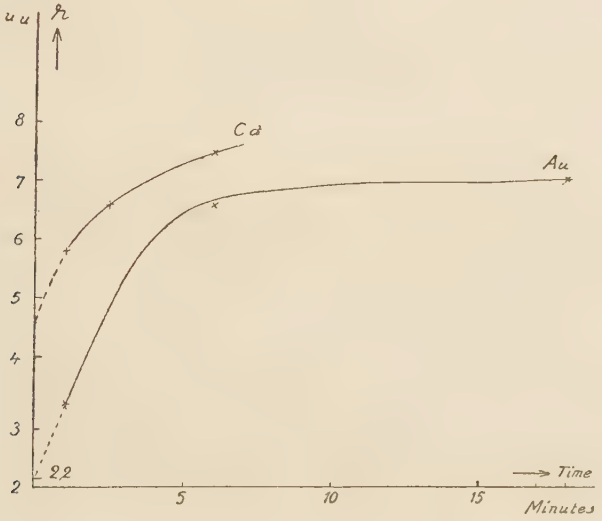

Fig. 24.

acetone was distilled with permanganate of potassium. Boiling point 56,45°. The ether was purified in the usual way, and afterwards distilled with sodium. The isobuthyl alcohol was distilled with calcium. The dispersion was carried out at — 75°. When determining the degree of dispersity of etherosols, the nuclear liquid cannot be added directly to the gold solution, as it does not dissolve rapidly enough. In order to hasten the rate of dissolving, I mixed the nuclear liquid with about its own volume of alcohol, before adding it to the gold solution. The method has been successfully employed on Pt-sols by Mr J. Lindeman at the laboratory of Upsala. On account of the instability of the etherosols, the values of r are probably too great. The

Table XLVIII.

$C = 3{,}2 \cdot 10^{-3}$ M. F. A = 0,20 — 0,25 mm. L = 0.

	Metal	I	c mg/cm³	t	K_1 ccm.	K_2 ccm.	T	v cm. 10^{-6} per sec.	r $\mu\mu$	r_k $\mu\mu$
Temp. — 75°	Au	1,2	0,023	1m	0,2	-	15,5	2,8	28	2,8
				2½	0,1	-	"	4,4	35	2,7
				1	0,2	5	15,8	16,5	68	2,9
	Pt	1,4	0,023	1½	0,5	10	15,0	9,4	52	3,8
				3	0,2	-	"	5,8	41	3,8
				4	0,1	-	"	8,4	49	4,1
	Zn	1,5	0,030	1½	0,2	5	"	6,3	43	2,9
				2½	0,5	2	"	11,4	57	3,9
				6	0,1	10	"	12,6	60	3,9
	Sn	1,2	0,076	1½	0,2	-	"	13,9	63	12,6
				3	"	-	"	"	..	..
				5	0,1	-	"	21	77	12,3
	Bi	1,9	0,11	12	0,1	-	15,6	38	103	17
Temp. + 17°	Au	1,2	0,030	1m	1	2	15,5	11,1	56	3,4
				3½m	1	5	"	24	82	6,7
				6m	1	5	"	"	"	6,7
				18m	1	5	"	26	86	7,1
				3h	1	5	"	32	95	7,8
				40h	1	-	"	7,1	46	8,3
	Au	1,6	0,80	9 months	0,1	5	14,7	29	91	10,3

results of the determinations of isobuthyl alcosols did not agree well. This may possibly be due to the exceedingly high viscosity of isobuthylalcohol at — 75°, which has the effect partly that the liquid, in spite of stirring, does not acquire a uniform concentration, partly that the volume of the nuclear liquid is somewhat undefined, as the liquid runs very slowly off the pipette. Among several observation series I have quoted the best one in Table LIV. The lowest value of r obtained was 7,5 $\mu\mu$, the highest 9,5 $\mu\mu$.

See Tables LIII, LIV and Figs. 24, 25.

47. *Remarks.* — The accuracy of the method employed by the author to determine the size of Au-particles in hydrosols,

Table XLIX W-sols.

$C = 3{,}2 \cdot 10^{-3}$ M. F. $L = 0$ $T = -70°$.

Metal	I	c mg per ccm.	t	K_1 ccm.	K_2 ccm.	T	v cm. 10^{-6} per sec.	r $\mu\mu$	rk $\mu\mu$
Cd	1,0	0,14	1m	0,5	5	15	8,7	50	7,1
			1½	"	"	"	"	"	7,1
			3	"	"	"	9,6	52	7,5
			9	"	"	"	9,3	51	7,3
			"	0,11	5	"	26	87	7,5
			2h	0,5	"	"	18,5	73	10,4
Au	1,4	0,065	1m	0,5	2	15,2	9,6	52	3,3
			2m	"	"	"	"	"	"
			3m	"	"	"	10,6	55	3,5
			6m	0,1	5	"	14,5	64	3,2
			3h	0,1	10	"	23	81	4,9
			22h	0,5	5	"	11,1	56	4,8

depends on all the particles being of the same size. In fact, the particles seem to sink at the same rate, as in the course of time they form a distinct boundary above which the liquid is clear. Such Au-hydrosols are generally dealt with by scientists as if they were monodisperse. The boundary mentioned only indicates, however, that the hydrosol contains no smaller particles than those of the limit layer, and accordingly it remains undecided whether the sol contains larger particles. In fact it very often occurs that if the hydrosol is cautiously poured out after some time, there is a sediment on the bottom, which, when shaken up, turns out to consist of larger particles than could be

Table L.

Cd. C-sol.

I	c	t	K_1	K_2	T	v	r	rk
1,0	0,19	1	1	5	16,0	13,2	61	12,0
		3	0,5	-	"	4,5	35	12,6
		7	0,25	-	"	6,6	42	11,7

Table LI.

Silver.

I = 1,5 Amp.

Temp.	c mg per ccm.	t	K_1 ccm.	K_2 ccm.	K_3 ccm.	T	v cm. 10^{-6} per sec.	r $\mu\mu$	r_k $\mu\mu$
+ 17°	0,080	5m ?	1	2	5	14,4	10,0	54	2,6
		30m	0,2	5	-	"	10,6	56	4,6
		22h	1	2	-	"	8,9	51	5,3
		"	0,25	5	-	"	11,5	58	5,1
— 40°	0,30	10m ?	0,2	1	5	14,8	22	79	2,7
		15m	0,04	1	-	"	12,6	61	2,7
		45m	0,2	1	5	"	26	87	3,0
		30h	0,2	1	5	"	27	88	3,0

expected from the falling velocity of the limit layer of the original hydrosol. It also happens that the hydrosol, after standing for about a day, is apparently more concentrated near the bottom than in the upper part of the vessel. In such cases I have rejected the determination. I have got the impression that the concentration at different heights must be very different to be perceived by the eye. I therefore conjecture that the particles may also be of different sizes if the sol seems homogeneous after a day. Still, according to the results in Chapter V, the sedimenting method is apparently as accurate as the method of counting particles under the ultramicroscope.

Table LII.

Gold.

I = 1,5 Amp.

Temp.	c mg per ccm.	t	K_1 ccm.	K_2 ccm.	K_3 ccm.	T	v cm. 10^{-6} per sec.	r $\mu\mu$	r_k $\mu\mu$
+ 17°	0,11	10m	1	2	5	15,0	10,2	54	2,3
		24h	0,2	1	-	"	9,1	51	2,3
— 40°	0,10	30m	1	1	5	15	16,5	69	2,3

Table LIII.

Au.

Degree of dispersity in different media.

$C = 3{,}2 \cdot 10^{-3}$ M F A = 0,25 mm.

Medium.	I	c mg per ccm.	t	K_1 ccm.	K_2 ccm.	t	v cm.10^{-6} per sec.	r $\mu\mu$	r_K $\mu\mu$	Remarks.
Ether	1,6	0,028	1m	0,5	5	15,5	9,8	52	3,35	
			2 »	"	5		16,3	68	4,33	
			4 »	"	5		18	71	4,56	
			8 »	"	-		4,1	34	4,80	
Acetone	1,2	0,025	1m	0,5	2	15,5	7,5	46	2,2	The gold so-
			2 »	"	"		6,8	43	2,1	lution con-
			3 »	"	"		"	"	2,1	tained only
			8 »	"	"		7,5	46	2,2	4,43 instead of
			11 »	0,1	5		10,4	54	2,0	4,93 mg. gold
			3h	0,5	2		26	86	4,1	per ccm.

With regard to the alcosols to be determined, the gilding method is not better than others, as we are as yet unable to take into consideration the possibility that the nuclei are of different sizes. But this must be admitted to be very probable, on account of the observations above regarding the sizes of the gilded particles.

The author has stated the degree of dispersity of the sols in terms of r, thus assuming a spherical shape of the particles. No evidence, however, has been offered of the truth of such an assumption. So we must bear in mind that the values of r have

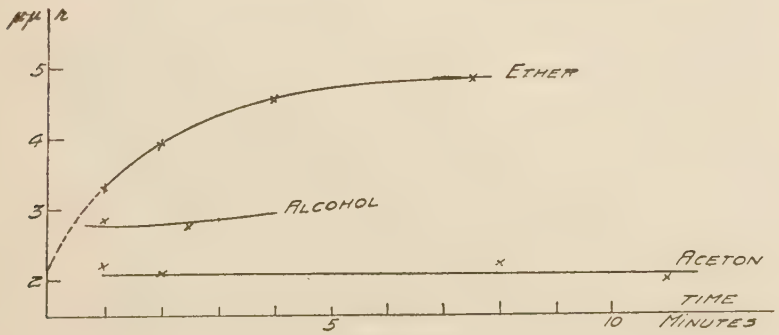

Fig. 25.

Table LIV.

Cd.

Degree of dispersity in different media.

$C = 3{,}2 \cdot 10^{-3}$ M F ' $A = 0{,}25$ mm.

Medium.	I	c	t	K_1	K_2	t	v	r	r_k
Ether	1,5	0,064	$1\frac{1}{2}$m	0,5	5	16,0	13,5	61	6,7
			$3\frac{1}{2}$m	0,5	-		6,3	42	10,1
			12m	The sol partly coagulated.					
Acetone	1,3	0,10	1m	0,5	2	16,0	11,5	57	5,4
			$2\frac{1}{2}$m	0,1	-		4,4	35	5,8
			12m	0,1	-		6,7	43	7,1
			30m	0,5	-		5,5	39	11,1
Isobuthyl-alcohol	1,2	0,031	3m	0,2	-	16,3	12,5	59	8,3
			16m	"	-		13,2	60	8,1
			18m	0,1	-		22	78	8,7

only an approximate signification, being the radius of a compact globule of the same mass as that of the particle. We shall discuss the matter in more detail in the next section. Though it cannot be decided to what extent the size of particles obtained by the gilding method corresponds to the actual extension of the

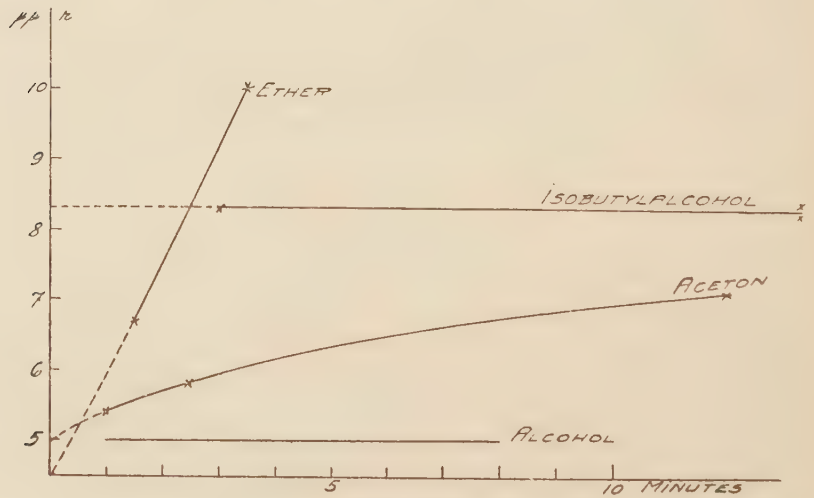

Fig. 26.

particles, the advantages of the method are conspicuous. In fact, whatever may be the meaning of r, the method offers a measure of the degree of dispersity which renders it possible to make comparisons between the sizes of particles of the same sol at different points of time as well as of different sols. In determining the degree of dispersity of sols of very low temperature, it should be observed that the volume of the nuclear liquid must be reduced to the temperature of the room. In order to find the factor of reduction required, the author put 0,5 ccm. alcohol of $-75°$ into a closed weighing glass by means of his pipette. Having attained the temperature of the room, the alcohol weighed

1) 0,417 g.
2) 0,412 »

Mean value 0,415 g. corresponding to a volume of 0,524 ccm. at the temperature of the room. Accordingly the volume was 4,8 per cent too great, which means an error of 1,6 per cent in the value of r. Now, in order to prevent the increase of the particles, the nuclear liquid must be added very rapidly to the gold solution, and so the volume of the nuclear liquid will not be exactly of the value intended. Besides, in determining the radius of the gold particles, the errors of observation are about 5 per cent. So the author has thought it unnecessary to consider the errors of r caused by the low temperature of the nuclear liquid.

48. *Instability of Electric Sols.* — As we have now obtained a means of determining the size of particles, let us define those sols as stable whose degree of dispersity is constant. The results of the determinations indicate that strictly speaking no sols are absolutely stable. Most of them, however, after increasing for some time reach a region of relative stability where they preserve their degree of dispersity for days or weeks. Au-sols are often of a constant degree of dispersity for at least one year. Moreover, Au-alcosols behave differently when produced at different temperatures. If produced at $-75°$, the sols remain constant when they reach the value of $r = 5\,\mu\mu$ (see Table XXXI, Section 38), if produced at the temperature of the room, the particles increase to the value of $r = 10\,\mu\mu$, after which the sols remain constant. A W-sol, produced at $-75°$, ceased to increase at the same value of r as that of the corresponding O-sol,

i. e. $r = 5\,\mu\mu$. On the other hand, it often occurs that Au-sols increase slowly beyond the limits given above. The sol in such cases coagulates in the course of time.

In the case of other alcosols I have not followed the size of particles for more than about one week. Old Cd-sols do not give good results, probably on account of the particles being too much oxidised. The results referring to Bi-sols, Table XLIII, indicate that after some days the increase is very slow. The same thing follows from the stability of the sols, which apparently lasts as long as they are preserved. In section 43 we have already pointed out the result that the initial rate of increase depends upon the concentration of the sol.

49. *Structure of Particles of Electric Sols.* — The increase of the particles, immediately after the dispersion, goes to show that the electric sols ordinarily contain only secondary particles. We shall now enter upon the question of their structure. Though the particles of a Bi-sol were of the size $r = 76\,\mu\mu$ (see section 38), they apparently did not settle to the bottom. Now this is very difficult to explain, unless one assumes that the particles are not compact, and what is more, one must conclude that they have a very loose structure. In this connection there is also another behaviour of Bi-sols to be considered. Only a small quantity of Bi-nuclei must be added to a gold solution; otherwise the hydrosol produced will be unstable. The results in Table XLIII show that the weight of the gold must be about 250 times as great as the weight of the Bi-particles, if the hydrosol produced is to be stable. Sn-sols and Cd-sols also behave in a similar way. Assuming a loose structure of the particles we can conceive a plausible explanation of this observation if we take into account the instability of alcosols of Bi and Sn, when poured into water. If the particles were compact, they would probably not require a very thick layer of gold to protect them from coagulating. On the other hand, if they are of a loose structure the gold molecules will, on reduction, penetrate into the Bi-particles, making the nucleus compact before producing the protecting layer round it. The data in table XLIII make it possible to calculate the real extension of the Bi-particles. On using 0,5 ccm. of the sol as a nuclear liquid the hydrosol coagulated, on using only 0,2 ccm. it did not. The latter quantity produced

a hydrosol of a radius 5 times as great (161 $\mu\mu$) as that of the Bi-particles (33 $\mu\mu$, assuming the mass to be compact). The former volume consequently would have produced particles of a radius that is $\sqrt[3]{\frac{0{,}2}{0{,}5}} \cdot 5 = 4$ times as great as the radius of the particles of the original Bi-sol (the mass compact). Now this means that the real Bi-particle is spread in a sphere of a radius 4—5 times as great as that of a compact Bi-particle of the same mass. Accordingly the volume occupied by the particle would be about 100 times the volume of a compact particle of the same mass. Thus the gilding method will perhaps make it possible to determine the real extension of ultramicroscopical particles of loose structure.

Let us consider the falling velocity of such a particle. Naturally the space between the primary particles must be filled with the disperse medium. Assume a particle of the extension described above, obeying Stokes' law. It can be calculated that a Bi-particle of radius 60 $\mu\mu$ (assuming the mass compact) would sink in alcohol at the same rate as a gold particle of an Au-hydrosol, 17 $\mu\mu$ in radius. Consequently it does not sink at all, which is in accordance with our experience. The behaviour of Au-alcosols also indicates that in some respects the particles are not of a very solid structure. We have stated in section 35 that the power of absorption of light possessed by Au-sols changes in the course of time, their colour changing from violet to red. The degree of dispersity remaining constant, it must be concluded that the particles themselves undergo a change. This could not, however, very well take place if the particles were initially of the ordinary compact structure.

50. *Structure of Particles Initially Present.* — With regard to the structure of the particles immediately after the pulverisation, we have to deal with the question as to whether they are primary particles or not. The results of the determinations go to show that the size of the particles is independent of current intensity, self-induction, and capacity. See Tables XLV—XLVII. Because of this one might be inclined to assume that the particles are primary ones. Yet the author is of the opinion that they are not. In fact, the results in Table XLVII and the last series in Table XLVIII, Fig. 24 show that particles produced

at the temperature of the room increase initially very rapidly.

Now the pulverisation must last about 30 seconds, a period which, according to the results, will be long enough to let a considerable portion of the particles increase during the process. Further, on extrapolating the values of r to the time $t = 0$, we see that the particles are certainly not larger, but probably smaller than if produced at $-75°$. This is very striking, as it would be natural to expect smaller particles at a low temperature of the medium. The matter will be clearer if we consider that also at a low temperature of the medium there must be a zone in the immediate vicinity of the electrodes where the medium has a temperature near its own boiling point. In the zone mentioned the rate of increase must be considerable, both on account of the high temperature and of the high concentration of the particles. Assuming that the particles increase before reaching the cold medium, we also arrive at a plausible interpretation of the results in Table XLV, according to which the particles are about 20 per cent larger than usual if a small length of arc is used. Under this condition the rate of dispersion is great, consequently the concentration near the electrodes is high. Moreover, a similar effect is caused by the short space between the electrodes giving no wide scope to the particles. The explanation above is supported by the results in Table XLIX, showing the size of particles of W-alcosols. When using the wave-current method, the rate of dispersion is high, the length of arc very small. Consequently according to the reasoning above, the particles must be expected to be larger than when using the O-current method. The size of the Cd-particles of O-sols being 5 $\mu\mu$, that of W-sols 7 $\mu\mu$, the results are in accordance with the reasoning above. In section 49 it has been stated that the blue or violet colour of a new Au-alcosol indicates a loose structure of the particles. Now the colour is generally of the same tone, whether the sol is produced at the temperature of the room or at $-75°$, so it must be concluded that in both cases the sol contains secondary particles.

In conclusion the author begs to call attention to some observations made during the process of dispersion. If the length of arc is small, it occasionally happens that the process suddenly stops. On increasing the space between the electrodes, there can

be seen a black thread or cloud of particles, connecting the electrodes. The thread being removed by knocking, the process begins again. The phenomenon is rather frequent in the wave current method. Moreover, when the process mentioned has been going on for some time, it often occurs that the edges of the electrodes are covered with a thick layer of coagulated particles. The author believes that the above observations verify the opinions suggested.

51. *Influence of Temperature and Viscosity of Disperse Medium.* — It has already been mentioned that the initial size of particles is likely to have a smaller value if a sol is produced at the temperature of the room than if produced at — 75°. This is evident from the determinations of an Au-sol, Table XLIII, Fig. 24. As a rapid cooling of a metallic gas would be expected to have quite the opposite effect, we cannot ascribe the influence on the size of the particles to the cooling effect of the disperse medium. I wish to propose another explanation of the surprising result of my experiments. According to the assumptions in the preceding section, the particles, before entering into the cold disperse medium, have to pass through a warm zone of high concentration of particles. In this zone the increase of the particles will depend upon the time they remain in the zone as well as on their concentration. Now if the liquid has a low viscosity the stirring effect of the bubbling of gas will be sufficient to drive the particles rapidly into the cool surrounding liquid. On the other hand if the liquid has a high viscosity, the bubbling of gas is less effective, the zone being surrounded by a viscous medium. Consequently the particles have to stay a rather long time in the warm zone. This must result in large particles entering the cold liquid. Hence it must be expected that the particles are larger when produced at — 75° than when produced at the temperature of the room. Now we will turn our attention to the influence of different disperse media on the degree of dispersity. On account of the instability of etherosols, the values of r are possibly too great. If we take this circumstance into consideration, the results in Tables LIII and LIV, on extrapolating the values of r to $t = 0$ (Fig. 25 and 26), show that the initial size of the particles will very probably follow the series:

Table LV.

Medium.	r $\mu\mu$		Molec. weight	Boil. point	Heat of vaporisation per gram	Viscosity			
	Au	Cd				T		T	
Ether	2	4,5	74	35°	94	0°	0,0030	30°	0,0022
Acetone. . . .	2	4,9	58	56°	140	"	0,0040	50°	0,0026
Ethylalcohol .	2,8	5,0	46	78°	237	"	0,0177	70°	0,0051
Isobuthyl-alcohol . . .	—	8	74	106°	130	"	0,0807	100°	0,0053

r of Isobuthylalcosol $> r$ of Ethylalcosol $>$.
$> r$ of Acetonosol $> r$ of Etherosol.

Table LV contains the approximate values of r at the time $t = 0$, as well as some constants of the media. It appears that the molecular weight cannot have any great influence on the initial size of the particles. In fact it seems to be very likely that the only constant of the medium that influences the size of particles is the viscosity. The table shows that the viscosities of the media at the boiling point do not differ very much. Consequently in the warm zone the influence of this constant cannot vary considerably with varying media.

On the other hand the viscosities at 0° are very different, and obviously the differences will be still greater at — 75°, at which temperature, for instance, isobuthylalcohol becomes viscous like pulp. On applying the argument proposed above the explanation of the results is obvious.

52. *Summary.* — The author has drawn the following conclusions from his investigations on the degree of dispersity of electric sols.

1) The stability of the sols is limited, the particles generally increasing with time. Au-alcosols are frequently stable for at least one year.

2) The rate of increase of the particles depends upon the concentration of the sol, being more rapid in a more concentrated sol than in a diluted one. At — 75° the particles of alcosols do not increase perceptibly, at least for the first few minutes.

3) On reaching a certain limit value of r, the particles begin to increase very slowly. The limit value of r is smaller when the sols are produced at a low temperature than when produced at the temperature of the room. If the particles extend beyond the limit value the sol soon coagulates. This action has been observed in Au-alcosols.

4) Particles of O-sols, W-sols, and C-sols have a loose structure.

5) The initial size of particles of O-sols is independent of capacity, self-induction and intensity. If the length of arc is very small, the radius of the particles produced is 20 per cent greater than ordinarily.

6) The particles of W-sols (r of Cd-particles $= 7\ \mu\mu$) are larger than those of O-sols (r of Cd $= 5\ \mu\mu$).

7) The particles present immediately after the dispersion are probably secondary particles.

8) The initial size of particles increases with the viscosity of the medium. The cooling of a liquid causing the viscosity to increase, the initial size of particles accordingly increases with a lowering of the temperature.

9) The initial radius of Cd-particles of a C-alcosol is 2,5 times as great as the radius of O-sol particles, their mass being consequently 15 times as great as that of O-sol particles.

10) S- alcosols of Ag change their degree of dispersity during the first few hours. When the sol is produced at a low temperature, the rate of increase is very slow. S-alcosols of Au are practically of a constant degree of dispersity. The initial size of particles of S-sols is not very different from that of O-sols.

PART III.

Nature of Electric Synthesis of Colloids.

CHAPTER VIII.

Formation of Melting Globules.

53. *Presence of Melted Metal and Melting Globules under Different Conditions.* — It has long been known that during Bredig's electric synthesis part of the electrodes are in a melted state. We have also found that during the dispersion a considerable part of the melted metal is scattered into the liquid. In one case the scattering effect failed, viz. when thick Cd-electrodes in a vertical position are pulverised by means of C-current. With regard to the effect of the C-current, experience tells us that undoubtedly the melted metal is split, but that in the case of thick electrodes the globules do not reach the liquid to any considerable extent before reuniting with the electrodes. If, however, the current is interrupted, e. g., 140 times per sec. (I-current, section 29) a sediment of melting globules will be formed. The sediment is of about the same quantity as that of O-sols.

Svedberg's method with the arc confined in a quartz tube also produces melting globules. As the liquid in the latter case cannot touch the electrodes, we must conclude that it is sufficient if a current of gas (nitrogen) passes the electrodes. Then part of the melting globules follow the current of gas into the liquid. Taking into consideration the oscillatory and the wave current methods, I will try to find the power that splits the melted metal into globules.

54. *Observations on the Influence of the Medium.* — It is tempting to assume, as Benedicks[1] has done, that at each break of the current the liquid, rushing with great speed against the electrodes, splits the metal and scatters the globules into the

[1] l. c.

surrounding liquid. But it is also possible to imagine other explanations of the melting globules. In fact the formation of melting globules by using Svedberg's method with the arc confined in a quartz tube goes to show that no extraneous force is necessary to produce globules. One is therefore reduced to the assumption that melting globules are formed exclusively by means of the energy of the electric current or of the energy of heat produced by electrical energy.

The author has tried to ascertain whether the liquid really rushes against the electrodes at each break of the current. Benedicks[1], in support of this hypothesis, has stated that between the electrodes there is a very great mechanical pressure, which in spite of the electrodes being carefully fixed to the micrometer, can occasionaly force them apart from one another. The author has examined the matter somewhat more closely. For this purpose the arc micrometer was partly altered, the holder for the upper electrode being replaced by another shown in Fig. 27. The electrode (Cd) was connected with the rod by a coil-spring, surrounded by a brass tube, in which the electrode could slide without resistance. A pressure of 1 g. lifted the electrode 0,1 mm. The electrodes were put into alcohol, and the space between the electrodes regulated to 0,1 mm. Watching the upper electrode through a microscope (magnification about 100 ×), I brought the oscillatory current into action. ($C = 3{,}2 \cdot 10^{-3}$ MF, $L = 0$). No movement of the electrode could be perceived.

Fig. 27.

I must consequently conjecture that the pressure observed by Benedicks is not a regular phenomenon, at any rate it seems to be very small. On the other hand it must be admitted that, the craters of the electrodes being small, the liquid can very well rush against the electrodes without producing any measurable pressure. At any rate, when using the wave current method it is obvious, from the following observations, that the liquid cannot at each interruption fill the space between the electrodes.

Benedicks[1] has referred to a statement of Simon's, according to which in the case of a short period of vibration the successive discharges issue from the same point of the electrodes during

[1] l. c.

a time that is long relative to the period of vibration. The wave current used by the author having 10^6 vibrations per sec., why should this happen if along the track of the arc there does not remain a residue of conducting matter, which would be excluded if at each interruption the liquid washed over the surfaces of the electrodes?

Moreover, as will be seen from the description below, the mere observation of the wave current arc gives rise to the conviction that the liquid cannot behave as has been assumed by Benedicks. If the length of arc is carefully regulated, the wave current arc burns quietly like a continuous current arc.[1] Only a feeble rustling, not unlike that of a C-current arc, announces the small bubbles arising from between the electrodes. If the electrodes are examined after the dispersion, there can often be perceived an outline dividing the surface into two fields of different aspects, see Fig. 28. The internal field is dim grey, on a closer examination turning out to be covered with small globules. The external one has a metallic brightness, showing that it has been washed over by the surrounding liquid during the process. Kohlschütter[2] has made a similar observation. Now it is true that in using the oscillatory current method I have not been able to perceive the outline described above. But if the length of arc is kept small the rustling during the process is as soft as that of the wave current arc. Now and then a crackling indicates that the process has been interrupted by the liquid filling the space between the electrodes. When the space between the electrodes is widened, the cracklings become more numerous, up to $A = 0{,}5$ mm. (Electrodes Cd), where only a strong crackling together with a violent sprinkling is perceptible. On warming up the disperse medium the process becomes calmer, and the crackling ceases. The maximum length of arc during the rustling process depends upon the material of the electrodes, the volatile metal Cd permitting twice as great a length of arc (0,5 mm.) as does Au (about 0,25 mm.). With regard to the wave current method, the author has measured the maximum

Fig. 28.

[1] Barkhausen, Jahrb. f. Drahtl. Telegr. u. Teleph. **1**, 243 (1907).
[2] V. Kohlschütter, Zeit. f. Electrochemie, **25**, 309 (1919).

Table LVI.

Maximum length of Arc. Wave current.
$I_c = 0{,}3$ amp. $C = 12{,}8 \cdot 10^{-3}$ M. F. $L = 1{,}00 \cdot 10^{-8}$ Henry.

Metal	I_1	V	I_2	A	Boiling point of metal
Sb	0,17	194	1,6	$6{,}0 \cdot 10^{-2}$	1300°
"	"	"	"	$5{,}0 \cdot 10^{-2}$	
Cd	"	"	"	$5{,}5 \cdot 10^{-2}$	780°
"	"	"	"	$5{,}5 \cdot 10^{-2}$	
Bi	"	"	"	$2{,}8 \cdot 10^{-2}$	1400°
"	"	"	1,65	$2{,}6 \cdot 10^{-2}$	
Au	"	"	1,65	$2{,}1 \cdot 10^{-2}$	2500°
"	0,15	220	1,65	$1{,}9 \cdot 10^{-2}$	
Pt	"	"	1,9	$1{,}0 \cdot 10^{-2}$	3000°
"	"	"	"	$1{,}1 \cdot 10^{-2}$	
"	0,14	234	2,05	$1{,}2 \cdot 10^{-2}$	

length of arc of different metals. The results are to be found in Table LVI. It appears that the maximum length of arc depends upon the material of the electrodes. Moreover the break of the wave current occurs at about the same voltage (V), independent of the material.

55. *Conclusions from Analysis of Pulverised Alloys.* — A decisive proof of the fact that the globules are not formed by the liquid splitting the melted metal is offered by the results in Chapter III obtained by analysis of pulverised alloys. If the melted alloy were split by the liquid it would be expected that all globules should be of the same composition. The analysis has shown that this is not the case, the finer sediment always containing more of the less volatile metal than the coarse one. Besides, the results in Table XVII show that the composition of the sediments is independent of the melting point diagrams, Fig. 5. We must therefore conclude that the particles must have existed, at least for some moments, in a zone of such a temperature that the volatile metal has had time to evaporate to a greater extent than the non-volatile metal.

[1] l. c.

I am inclined to a certain extent to accept the opinion of Kohlschütter[1], according to which the globules seem to behave as a sort of »Mittelleiter» between the electrodes. On the other hand, I cannot share his opinion that the globules are formed in the same way as the very small particles, i. e. by recondensation, on account of the results obtained by registration and by the analysis of dispersed alloys. I believe that the origin of the melting

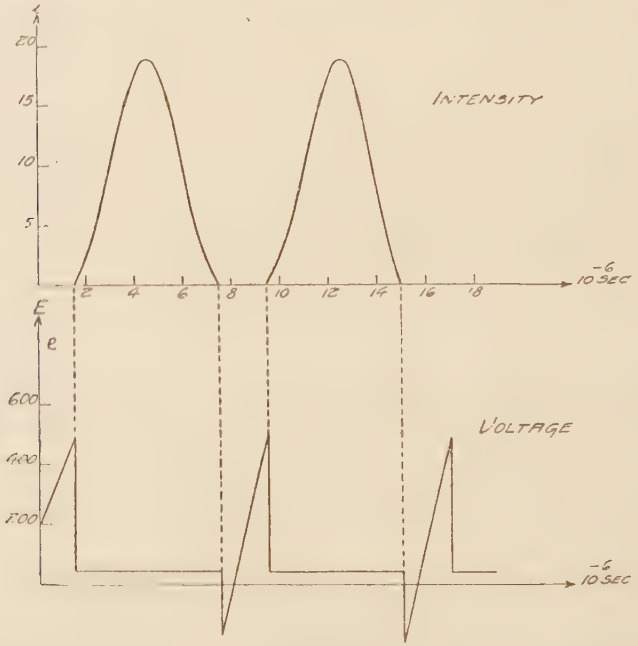

Fig. 29.

globules must be sought partly in the electric force itself, partly in the electrical energy transformed into heat, and I shall try to explain their formation.

56. *Explanation of Splitting Process.* — At the beginning of an oscillatory period when the intensity is 0, the voltage, on the contrary, has its maximum value. The current increasing, the voltage sinks rapidly and is then nearly constant until the current intensity has sunk to zero. The diagram Fig. 29 illustrates the conditions according to Barkhausen[2], who has made his investigations on undamped oscillations of high frequency (wave current).

[1] l. c.

[2] l. c. 247.

The vibrations of the oscillatory current, it is true, are damped. Yet the author considers this fact to be of subordinate importance in this connection. Now we can conceive the process as follows.

When the voltage has reached its maximum value the electrodes will have become so hot that the current breaks loose with great violence, metallic gas acting as a carrier of the electric charge. One part evaporates directly owing to the electric pressure, the other part evaporates owing to the high temperature of the melted metal. Consequently there arises one evaporation by electricity (surface tension »Zweiter Art» of Wo. Ostwald), and another evaporation by heat. The »fountain» of metallic gas will sweep away part of the melted metal, which will form drops between the electrodes where they act as the »Mittelleiter» of Kohlschütter. In so doing they will perhaps partly evaporate and if they are alloys they will consequently lose more of the volatile metal than of the other. This will happen especially to the small drops, as the large ones cannot float in the gas for any length of time. We have assumed above that, according to the opinion of Duddell[1] and others, the conduction of electricity in the arc is an electrolytic one.

[1] W. Duddell, Phil. Trans. **203** (A), 305 (1904).

CHAPTER IX.

Formation of Sols Proper.

57. *Different Zones Between and Near Electrodes.* — In order to fix our ideas let the sphere between and near the electrodes be divided into three zones; see Fig. 30. The central zone (I), »the arc zone», filled with vapors of metal, is surrounded by zone II, where the medium is in a gaseous state and where its decomposition also takes place. I will call zone II »the heat zone». Outside that zone, between and in the immediate vicinity of the electrodes, there is a territory which, on account of the heat gas ascending along the electrodes, will be rather warm. This territory may be called »the warm or bubbling zone». So, before reaching the cold liquid, the metal has to pass through all three zones.

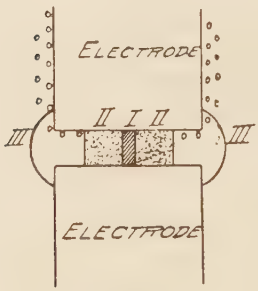

Fig. 30.

58. *Production of O-sols and W-sols.* — Let us consider Svedberg's oscillatory method. When the arc goes out the metallic gas will be condensed, entirely or in part. On account of the very short period of vibration, less than 10^{-6} sec., we can assume that only very small particles are formed and that part of the gas remains uncondensed until the next ignition produces an explosion of fresh metallic gas, which will force apart the particles previously formed. As the process continues the particles will be driven farther apart and will then follow the gaseous decomposition products until they are caught by the liquid. It is easy to ascertain that the bubbles of gas contain metallic particles, as when ascending to the surface they produce a tiny cloud which can be caught on a glass plate. Starting out from the assumption that while the arc is in its stable state the arc zone must be filled with gas of metal, there is no reason to conjecture that the particles produced on the break of the current will differ

in size under different experimental conditions, as long as the experiments can be explained in a simpler way. So we will assume that the size of the particles at their entrance into the heat zone is tolerably independent of capacity, intensity, self-induction, and length of arc. First let us try to examine whether the particles have time to unite to any considerable extent while passing through the heat zone. If we take into account the fact that the particles must follow the decomposition products of the medium, it is possible to estimate the order of magnitude of the interval of time under which the particles are in the heat zone. We will calculate the interval mentioned under the conditions $C = 3{,}2 \cdot 10^{-3}$ MF., $I = 1{,}13$ amp., $L = 100 \cdot 10^{-8}$ Henry, $A = 0{,}25$ mm. According to Table XIX 23,5 ccm. of gas per min. will be produced in this case. Let the volume of the heat zone be v. Since 23,5 ccm. of gas ascends from between the electrodes per min., the volume, v, will be replaced by a fresh quantity of gas every

$$\tau = \frac{v}{23{,}5} \cdot 60 \text{ sec.}$$

Assume for a moment the zone to be something like a cylinder, 2 mm. in diameter and 0,25 mm. (space between the electrodes) in height. Consequently

$$v = \pi \cdot 1 \cdot 0{,}25 = 0{,}8 \text{ mm}^3.$$

$$\tau = \frac{0{,}8 \cdot 10^{-3}}{23{,}5} \cdot 60 = 0{,}002 \text{ sec.}$$

Of course we do not assert that the assumed volume of the heat zone is the real one, but at any rate it must be of the same order of magnitude as has been calculated. Accordingly it can be conjectured that the particles are in the heat zone for only a very short time before reaching the liquid. So we can conceive the reason why the particles do not acquire any considerable size when passing the heat zone. Moreover it can be observed that the molecular weight of the disperse medium seems to have no influence on the initial degree of dispersity (see Table LV), which it has, according to Kohlschütter[1], if the process is slow. So we must assume that the particles are still very small when they reach zone III, the bubbling zone. Immediately before reaching the bubbling

[1] V. Kohlschütter, Zeit. f. Electrochemie, **18**, 373 (1912).

zone there will be condensed on the particles a thin layer of the least volatile decomposition products, each particle acting as a condensing nucleus. On entering the warm zone the particles will continue to unite, and on account of the viscosity of the liquid they will gather to a rather high concentration. In section 49 we have found it probable that the amount of increase will depend upon the viscosity of the medium, as the time for which the particles are in the zone will increase with the viscosity. Now assume the medium and its temperature to be unchanged. Then the rate of increase will depend upon the concentration of the particles as well as upon the length of the time for which they remain in the warm zone. Soon after the beginning of the process the concentration of the particles will have reached its stationary value. This value must in some way depend upon the rate of dispersion and also upon the rate of decomposition, since the latter produces the stirring of the liquid. The higher the rate of dispersion, the higher the concentration, and, on the other hand, the higher the rate of decomposition, the lower the concentration. Therefore let us take the value of $\frac{m}{v_o}$ (m = rate of dispersion in mg. per min.; v_o = rate of decomposition in ccm. per min.) as a certainly very approximate measure of the concentration and accordingly of the rate of increase of the particles in the warm or bubbling zone (as well as in the heat zone). In Table LVII are to be found the values of $\frac{m}{v_o}$, calculated from Svedberg's determinations under different conditions (l. c. Table XIV, page 39; Fig. 21 page 54; Table XXI and XXII page 55). Svedberg has determined the value of $\frac{v_o}{m}$ where m means the total quantity of dispersed metal. In our case, however, we must mean by m only the condensed portion of the metal. In the Table the values of $\frac{m}{v_o}$ are corrected with reference to the percentage of sediment. The Table also contains the average value of r for the corresponding Cd-alcosols.

It appears that the values of r increase with $\frac{m}{v_o}$, which is in accordance with the reasoning above. Besides it seems that the length of arc has an influence of its own, as determination no.

Table LVII.

No.	C M. F.	A	v_o/m	m/v_o Calc.	r $\mu\mu$	Current
1	$0{,}4 \cdot 10^{-3}$	0,25	2,3	0,35	5,3	O
2	$1{,}6 \cdot 10^{-3}$	"	1,9	0,37	5,1	"
3	$3{,}2 \cdot 10^{-3}$	"	1,5	0,39	5,0	"
4	$12{,}8 \cdot 10^{-3}$	"	0,7	0,7	5,4	"
5	$90 \cdot 10^{-3}$	0,05	0,3	1,5	6,2	"
6	$3{,}2 \cdot 10^{-3}$	0,05	1,0	0,6	6,3	"
7	$3{,}2 \cdot 10^{-3}$	Small		0,51	7	W
8	"	0,25		0,26	5	O

6 presents a higher value of r than no. 4 in spite of the value of $\frac{m}{v_o}$ being equal.

In Chapter VII we stated that the particles initially present in the cold medium are probably of a loose structure, judging from the fact that the gold sols have not the usual red colour of sols of a high degree of dispersity. The fact that the particles on uniting do not form compact ones is probably due to the layer of the decomposition products on the particles produced in the heat zone preventing the particles from uniting intimately. The influence of the layer would thus correspond to Zsigmondy's observation, according to which gold solutions in not absolutely pure water do not produce red sols but blue ones.

59. *Formation of S-sols.* — If the electric synthesis of colloids answers in the main to the proposed explanation, it would be expected that the particles that increase in the heat zone would form compact ones, as they have not yet been covered with a layer of decomposition products. So, if we reduce the warm zone to a minimum, or if in some way we could prevent the particles from touching the medium gas before being cooled to a certain degree, we may expect the particles produced in the liquid to be compact, the consequence of which is that an Au-sol would be red. Now that is what Svedberg has managed to do by his new method with the arc confined in a quartz tube. The arc being surrounded by the nitrogen current, which blows the substance out through the hole of the tube, the particles can

hardly touch the gas of the disperse medium before being cooled, which is apparent from the spectra reproduced by Svedberg. Besides, the stirring is so intense that it must be doubted whether the warm zone exists at all. So, in conformity with the explanation above, the particles must be expected to produce a red sol, which is in fact the case, according to Svedberg's statement.

60. *Formation of C-sols.* — It remains to be explained why Bredig's method produces larger particles than other methods, in spite of the fact that the value of $\frac{m}{v_o}$ must be much less in Bredig's method than in the others, the rate of decomposition being higher. In the case of Bredig's method no interruptions cause a total condensation of metallic gas, nor do any explosions drive out the particles condensed. So we may conclude that the condensation takes place only at the surface of the arc, where the heat zone is in contact with the arc. Before reaching the liquid the particles will gather between the electrodes near the arc in a relatively high concentration, and moreover they will have more time to unite than if the current is oscillating. The consequence of this would be that Bredig's method must produce larger particles than the oscillatory current or wave current methods.

61. *Closing remarks.* — According to the explanation of the electric synthesis of colloids it might be expected that the »cathodical hard» metals would produce the smallest particles, which on the whole is in accordance with the results in Chapter VII. Still there are differences, which must as yet be ascribed to specific properties of the metals investigated. I have not pursued the subject further because of the lack of completeness in the material for the experiments.

The treatise now concluded has proved that electric sols are produced by condensation of gaseous metal. Summing up the results obtained, I have endeavoured to suggest an image of the electric synthesis of colloids which will explain the results of the experiments in a natural way. The defectiveness of the image is obvious. As is always the case with the first attempts to solve a problem, the ideas suggested in this dissertation have been schematised in order to obtain a survey of the subject. The author is therefore conscious that his theories require correction in more than one respect.